



PM_{2.5} and PM_{10-2.5} Compositions during Wintertime Episodes of Elevated PM Concentrations across the Midwestern USA

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ABSTRACT

Northern cities in the Midwest experience frequent PM concentrations in excess of the Federal PM_{2.5} and PM₁₀ National Ambient Air Quality Standards (NAAQS) during winter, which increasingly outnumber the summertime excesses the further north the cities are located. In contrast, cities located south of the Great Lakes tended to experience a greater number of excesses during summer. In order to ascertain the key components of PM contributing to these winter exceedances, we examined a regional elevated PM concentration episode which occurred between January 31, 2005 and February 6, 2005. The episode was caused by meteorological stagnation which affected 9 states in the Midwestern US (MN, WI, MI, IA, IL, IN, OH, MO, and KY). The temporal and spatial characteristics of PM_{2.5} and PM_{10-2.5} mass and bulk chemistry (nitrate, sulfate, ammonium, organic matter) were measured during this and other wintertime elevated PM episodes at Milwaukee, WI, and compared to Chemical Speciation Network (CSN) data. The observed elevated PM episodes demonstrated that nitrate was the driving anthropogenic component of the wintertime exceedances. This led to the conclusion that winter NO_x controls on mobile and stationary sources, in combination with sufficient SO₂, VOC and NH₃ controls, should be further examined for the mitigation of wintertime PM_{2.5} episodes in the Midwest. The north-south gradient in exceedances of the PM_{2.5} NAAQS indicated that strategies for avoidance of violations of the 24-hour standard, and to a lesser degree the annual standard, would benefit from an emphasis on different seasons, and therefore different PM components, depending how far north or south the city is located in the Midwest.

Keywords: Aerosol; Air pollution; Nitrate; State implementation plan; EPA.

INTRODUCTION

Particulate matter less than 2.5 µm in diameter (PM_{2.5}) is harmful to human health, and has been linked to morbidity and mortality caused by cardiac and respiratory illnesses (Dockery *et al.*, 1993; Pope, 2000; Peng *et al.*, 2005; Pope, 2007). However, the scientific understanding of how different PM_{2.5} components compromise human health is still an area of active research (Bell *et al.*, 2008; Franklin *et al.*, 2008; Valavanidis *et al.*, 2008; Bell *et al.*, 2009; Lauer *et al.*, 2009; Peng *et al.*, 2009). National Ambient Air Quality Standards (NAAQS) for PM_{2.5} were introduced in 1997, and revised in 2006, to limit the total mass concentrations to protect human health and welfare. At the time of this study

PM_{2.5} NAAQS were as follows: i) the 98th percentile of 24-hour averaged mass concentrations over a 3-year period were not to exceed 65 µg/m³, and; ii) the 3-year average of the annual means were not to exceed 15 µg/m³. However, the PM_{2.5} 24-hour limit was revised to 35 µg/m³ in December 2006, and stands as the current standard. The winter episodes of elevated PM reported in this paper, although made in 2004 and 2005 before the 2006 revision, will be interpreted in the context of the current standard to inform current and future air quality strategies.

PM less than 10 µm, but greater than 2.5 µm in diameter (PM_{10-2.5}; “thoracic PM”) has also been shown to affect health in the short-term while long-term effects are yet to be confirmed (Brunekreef and Forsberg, 2005; Lin *et al.*, 2005; Bai *et al.*, 2007; Yeatts *et al.*, 2007; Williams *et al.*, 2008; Zanobetti and Schwartz, 2009). Regulations for PM_{10-2.5} were proposed in the 2006 revision of the PM NAAQS but were ultimately postponed. PM₁₀ has been regulated since 1987 but includes PM_{2.5} and so is different than PM_{10-2.5}. PM₁₀ concentrations must not exceed a 24-hour average of

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150 $\mu\text{g}/\text{m}^3$ more than once per year, over 3 years (Williams *et al.*, 2008).

If any of these standards are not met the US Environmental Protection Agency designates the county in question to be in non-attainment of the NAAQS based on the previous 3 years of monitoring data. The State is then required to implement a plan of action in response. Attainment strategies focus on methods of reducing PM concentrations in the violating counties. Ideally, the responsible State agency would reach a robust scientific understanding of source-receptor relationships for PM in their jurisdiction from which to develop an implementation plan. To this end, the agency collects as much information about the factors contributing to non-attainment as resources allow, including: i) during which seasons, months, days of the week, hours of the day exceedances tend to occur; ii) which PM sources are important contributors to elevated concentration episodes; iii) whether sources of elevated $\text{PM}_{2.5}$ and PM_{10} concentrations are local or regional; and, iv) which sources are responsible – i.e. stationary sources (industrial, residential), and/or mobile sources (such as motor vehicles). The physical and chemical characteristics of particulate matter can be combined with knowledge of source inventories, meteorology, and atmospheric physical and chemical processing to improve, if not complete, the understanding of these source-receptor relationships (Fraser *et al.*, 2000; Pekney *et al.*, 2006), from which mitigation strategies can be developed.

The bulk chemical composition of atmospheric particulate matter measured in urban areas varies primarily due to differences in sources, atmospheric processes, the prevailing meteorology of the urban area, and the season of measurement (Malm *et al.*, 2004). Analysis of data collected by the Federal Reference Method Network (which provides PM mass measurements for NAAQS attainment assessments), and the EPA Chemical Speciation Network (CSN; previously called the Speciation Trends Network, STN) between 2000 and 2007 revealed that more exceedances of the PM NAAQS were observed during winter months than during summer months in the northern cities in the Midwest (Table 1). These winter episodes were often associated with high concentrations of nitrate (Figs. S1–S8; (Chu, 2004; Fischer and Talbot, 2005)). In contrast, exceedances at more southerly cities in the project study area (bounded by Saint Louis, MO and Louisville, KY) were more frequent during the summer and were associated with higher concentrations of organic carbon (OC) and sulfate (Fig. S1–S8).

Bell *et al.* (2008) observed the largest increase in hospital visits due to cardiovascular and respiratory illnesses during winter in the most populated counties of the northern US. Peng *et al.* (2005) observed increased PM related mortality during late winter and spring in Chicago and Detroit. Nitrate was not identified individually as a correlating factor with health degradation by Bell *et al.* (2008) and the physiological role of nitrate, if any, remains unidentified (Bell *et al.*, 2008; Franklin *et al.*, 2008; Valavanidis *et al.*, 2008; Bell *et al.*, 2009; Lauer *et al.*, 2009; Peng *et al.*, 2009).

During the week of Monday, January 31, 2005 through Saturday, February 6, 2005 a high particulate matter episode occurred across the Midwestern region of the United States, of which we studied the following 9 states: Minnesota, Wisconsin, Michigan, Iowa, Illinois, Indiana, Ohio, Missouri, and Kentucky. The meteorology of the episode was characterized by the Lake Michigan Air Directors Consortium (LADCO, 2009) as being precipitated by widespread meteorological stagnation due to a long lasting high pressure system. The system often produced strong temperature inversions and reduced mixing heights, and the associated reduction in air space ventilations rates in many urban centers allowed pollutant concentrations to increase above normal levels. As a consequence PM concentrations increased beyond typical levels, and the $\text{PM}_{2.5}$ 24-hour limit during the study (65 $\mu\text{g}/\text{m}^3$) was exceeded in St Paul, MN, and Detroit, MI. However, under the 2006 revision of the $\text{PM}_{2.5}$ 24-hour NAAQS, the PM concentration at many more Midwestern cities exceeded the revised limit of 35 $\mu\text{g}/\text{m}^3$, so future episodes of this kind may be important to air quality strategies (Table 1). As the 65 $\mu\text{g}/\text{m}^3$ limit is now obsolete we chose to use the 35 $\mu\text{g}/\text{m}^3$ limit in Table 1 to facilitate future planning.

The goal of this study was to arrive at a scientific understanding of the main components of $\text{PM}_{2.5}$ during winter elevated PM episodes in the Midwest, and thereby gain insight into the source contributions of these components. This study is intended to help State agencies tasked with reversing current and future non-attainment designations for $\text{PM}_{2.5}$ in the Midwest. PM component contributions to winter elevated PM episodes were evaluated by comparing the chemical composition of PM intensively studied during the February 2005 episode at Milwaukee, WI with multiple years of routine monitoring measurements at Milwaukee and other cities covered by the EPA Chemical Speciation Network in the Midwest.

METHOD

Sample Collections

This study used measurements of atmospheric PM made by UW-Madison during 2004–2005, and by the EPA Chemical Speciation Network between 2000 and 2007 (CSN; formerly the Speciation Trends Network, STN). The methodology and data archives of the EPA CSN are publicly available (USEPA, 2008), and so will not be described in detail here. Analyses of major ions (nitrate, sulfate, and ammonium), organic carbon, elemental carbon, and minor ions (sodium, potassium, magnesium, calcium, and chloride) were made on PM collected by UW-Madison. Analogous data were obtained from the EPA CSN database to extend the UW-Madison data set at Milwaukee to previous years, and to other cities around the Midwestern US during the high concentration episode.

UW-Madison Measurements

Samples of atmospheric particulate matter were collected over 24-hours from midnight to midnight on the EPA 1-in-6

Table 1. A comparison between the number of times PM_{2.5} concentrations (Federal Reference Method) were larger than NAAQS PM_{2.5} concentration limits during winter and fall, and during spring and summer in the largest cities in this study. In this table "excesses" means that the measured concentration was greater than the NAAQS to which it is being compared, and is not intended to imply anything about the attainment or non-attainment designations that EPA apply to monitoring sites. The data analysis in this table does not reflect the data analyses performed to determine attainment of the PM NAAQS. The purpose of comparing the number of individual days with concentrations greater than either the 24-hour or annual NAAQS is solely to illustrate the seasonal distribution of elevated concentration events to inform air quality strategies. The data sets typically start at the end of 2000, or the beginning of 2001, and finish at the end of 2007. Table 1a provide site and data quality information, Table 1b provides statistical analyses of NAAQS exceedances.

Table 1a

Site Information				Date Information				
Location	Site Number	Latitude	Longitude	Start Date	End Date	Number of Measurements	Winter and Fall Date Coverage	Spring and Summer Date Coverage
Minneapolis, MN	270530963	44.95366	−93.25821	1/7/2001	12/29/2007	722	91%	93%
Milwaukee, WI	550790026	43.061111	−87.9125	12/14/2000	12/29/2007	815	92%	93%
Detroit, MI	261630001	42.22862014	−83.20820002	12/20/2000	12/29/2007	985	95%	96%
Chicago, IL	170310076	41.75139998	−87.71348815	5/22/2001	12/29/2007	848	90%	93%
Cleveland, OH	390350038	41.476944	−81.681944	12/26/2000	12/29/2007	348	93%	93%
Indianapolis, IN	180970078	39.811097	−86.114469	12/20/2000	12/29/2007	691	90%	93%
Cincinnati, OH	390610040	39.128611	−84.504167	1/4/2004	12/26/2007	251	92%	99%
Saint Louis, MO	295100085	38.6563	−90.1981	2/9/2000	12/29/2007	932	97%	98%

Table 1b

Location	Winter and Fall (Oct–Mar)		Spring and Summer (Apr–Sep)		Annual		24hr	
	Days in excess of the annual PM _{2.5} NAAQS (15 µg/m ³)	Days in excess of the 24-hr PM _{2.5} NAAQS (35 µg/m ³)	Days in excess of the annual PM _{2.5} NAAQS (15 µg/m ³)	Days in excess of the 24-hr PM _{2.5} NAAQS (35 µg/m ³)	% of excesses in Winter	% of excesses in Summer	% of excesses in Winter	% of excesses in Summer
Minneapolis, MN	61	1	42	0	59%	41%	100%	0%
Milwaukee, WI	136	12	102	4	57%	43%	75%	25%
Detroit, MI	181	11	192	12	49%	51%	48%	52%
Chicago, IL	207	10	163	9	56%	44%	53%	47%
Cleveland, OH	83	8	79	13	51%	49%	38%	62%
Indianapolis, IN	127	5	164	14	44%	56%	26%	74%
Cincinnati, OH	40	0	57	6	41%	59%	0%	100%
Saint Louis, MO	170	6	199	13	46%	54%	32%	68%

day schedule between June 2004 and May 2005, with daily samples collected during the high PM episode (January 28–February 9, 2005). All sample collections were performed by UW-Madison. The sample collection site was located in Milwaukee, WI on the roof of a two story building north of downtown approximately 3/4 of a mile from Lake Michigan (2114 E. Kenwood Blvd, Milwaukee, WI; 43°06'29"N, 87°53'02"W). Three colocated medium volume PM sample collectors were used during both the 1-in-6 day and intensive sample collections: two PM_{2.5} channels and one PM₁₀ channel. The samplers used the internals employed in the URG 3000B (URG Corp., Chapel Hill, NC) and were housed in a custom made box with a common timer. The PM_{2.5} and PM₁₀ samplers were essentially the same except for a different cyclone on the inlet and a slightly different flow rate; 8 LPM for PM_{2.5} vs. 6 LPM for PM₁₀. Observed differences between PM₁₀ and PM_{2.5} semi-volatile species such as nitrate were thought to be dominated by the difference in size cut. If the higher face velocity of the PM_{2.5}

sampler were to have caused losses of nitrate that did not occur in the PM₁₀ channel, a consistent or at least frequent nitrate component to PM_{10-2.5} would be expected throughout the year. In contrast, the observations discussed later only showed a PM_{10-2.5} nitrate component during episodes of elevated PM concentrations.

All sampler surfaces in contact with the sample stream were coated in high-density cross-linked Teflon (URG Corp.). These surfaces were pre-cleaned with warm soapy water (Neutrad, Decon Laboratories, King of Prussia, PA) and rinsed with the following solvents in the order shown: 1) de-ionized water (18.1MΩ resistance); 2) hexane, and; 3) acetone. The sampler parts were allowed to dry in a fume hood under clean room wipes overnight before reassembly.

Samples were collected on six different substrates during each of the 1-in-6 day and intensive measurements (Table 1). Teflon and quartz filters were used in each of the three channels during the 1-in-6 day measurements and during the intensive collections. Quartz filters were prepared by baking

at 550°C in an oven for 15 hours and stored in Petri dishes lined with pre-baked foil. All Petri dishes were sealed with Teflon tape before and after sample collection. All sample substrates, and internal surfaces of the samplers were handled using clean techniques. Once collected, samples were stored at –20°C before and after shipment to UW–Madison, which was performed at 0°C.

An intercomparison of PM_{2.5} mass measurements made by the two UW–Madison sample collectors over the entire measurement campaign is presented in Fig. S9. An analogous intercomparison between the UW–Madison and EPA sample collectors is presented in Fig. S10. A very good agreement was observed between the UW–Madison sample collectors (slope = 0.99, r-squared = 0.99) including during the high PM concentration episode between January 31 and February 6, 2005. The comparison between the EPA and UW–Madison sample collectors showed a 13% bias to higher masses in the EPA sampler (slope = 0.87), and lower r-squared (0.93) that was observed between the UW samplers. Comparisons of UW and EPA measurements of mass as a function of relative nitrate content (r-squared 0.4) indicated this bias was due to insufficient temperature control in the UW sampler at ambient temperatures greater than 5°C; excess heat from the pumps caused more evaporative losses in the nitrate fraction of the PM collected on the filters than was observed in the EPA samplers at colder temperatures. However, as temperatures dropped below 5°C the discrepancy between samplers diminished to those seen above 15°C despite significant nitrate contents. This problem was avoided in the EPA sampling methods: i) the Federal Reference Method required sampler box be maintained within few degrees of ambient temperature, and; ii) the STN method physically isolated the sample media from sources of heat in the sampler. The maximum concentration day during the high PM concentration episode (see triangular data point in Fig. S10) demonstrated a bias towards higher mass concentrations in the UW sample collector, which measured 55 µg/m³, compared to the EPA sampler, which measured 43.6 µg/m³. On this particular day, the UW sampler did not operate for the full 24-hours, whereas the sample collected by the EPA sampler spanned the entire day. The discrepancy observed may have been caused by the UW sampler not collecting sample during a

portion of the day during which PM concentrations decreased. Since the EPA sampler continued to collect sample during this period of cleaner air, the average concentration measured by the EPA sampler would have been lower when compared to that measured by the UW sampler.

A relationship between PM₁₀ masses and PM_{2.5} masses was observed which when fitted with a least squares regression giving a slope of 0.79 with an r-squared of 0.91. The arithmetic mean ± standard deviation, and the geometric mean ± standard deviation of PM_{2.5}:PM₁₀ ratios were 0.68 ± 0.20, and 0.65 ± 1.34 respectively. The general distribution of mass between the regulatory size fractions did not change appreciably during the high concentration PM episode when compared with the rest of the year.

Sample Analyses

Atmospheric PM samples were analyzed for major and minor ion contents (nitrate, sulfate, and ammonium; sodium, potassium, and chloride, respectively) using ion-chromatography. Organic carbon and elemental carbon were measured using a thermal-optical method (Table 2).

Measurements of ions were made using samples collected on the Teflon filter substrates during the 1-in-6 day collections, while samples collected on quartz substrates were used for the ion measurements during the intensive collections. Samples were prepared for ion chromatographic analysis by wetting the samples and collection substrates with 0.3 mL isopropyl alcohol, submerging them in 30 mL of Milli-Q water in polypropylene centrifuge tubes, and mildly shaking for 3 hours at room temperature. For every 10 samples analyzed measurements were made on the extract from an analytical blank filter, which had not been previously handled after the initial cleaning in any way. Anions and cations were analyzed on sister ion chromatographs (IC), both Dionex ICS 1000 employing suppressed conductivity detection. Anions and cations were separated with Dionex separation and guard columns: anion separations used columns AS4A-SC and AG4A-GC; cations were separated using columns CS12A-SC and CS12A-GC. Analysis protocols for anions were developed from EPA 300 and NIOSH 7903, while cation protocols were based on OSHA ID-188. The IC was calibrated using initial and

Table 2. Information concerning sample collections at Milwaukee, WI conducted by UW–Madison: particle size cut of the inlet; sample collection substrate; average flow rate through the sample channels; and, suite of measurements performed on each filter.

Sample Collector	Nominal Particle Size	Filter Media (47 mm)	Average Flow Rate	Analysis
A&B	≤ PM _{2.5}	Teflon	5.97 ± 0.02	Mass, SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , Na ⁺ , Cl ⁻ , and K ⁺
C	≤ PM ₁₀	Teflon	7.90 ± 0.02	Mass, SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , Na ⁺ , Cl ⁻ , and K ⁺
A&B	≤ PM _{2.5}	Quartz	6.11 ± 0.04	Organic Carbon, Elemental Carbon (SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , Na ⁺ , Cl ⁻ , and K ⁺) ^a
C	≤ PM ₁₀	Quartz	7.70 ± 0.02	Organic Carbon, Elemental Carbon (SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , Na ⁺ , Cl ⁻ , and K ⁺) ^a

^a-during intensive measurements of the February 2005 PM episode only.

continuing calibration verification standards: analytical blank filters spiked with aqueous standard solutions of sulfate, nitrate, phosphate, chloride, sodium, potassium, and ammonium ions.

Measurements of the organic carbon and elemental carbon contents of the PM were made with a thermo-optical analyzer (Sunset Laboratory Inc. Forest Grove, OR) which has been described in detail previously (Schauer *et al.*, 2003). The analyzer was operated using the NIOSH 5040 method using 1.5 cm² punches excised from the quartz sample substrates.

EPA Measurements

To provide a historical context of the PM mass and composition measurements presented in this study we examined all EPA CSN data publicly available from the start of monitoring (winter 2000–spring 2001) at the cities listed in Table 3 (USEPA, 2008). The data examined were summarized in Figs. S1–S8. To provide greater temporal and spatial resolution of the mass and composition of PM during the February 2005 PM episode we downloaded data from the EPA Criteria Pollutants Monitoring Network and the EPA CSN network databases for the locations listed in Table 3 (USEPA, 2008). The PM_{2.5} collected by the Chemical Speciation Network was analyzed by the EPA for

ions, OC, EC and mass using the same techniques as used by UW-Madison. Differences existing between the methods for ions were minimal and were not expected to cause significant differences in results. OC and EC were measured by NIOSH 5040 with a Sunset Labs OCEC analyzer by both organizations. Collected mass was determined by pre- and post-collection gravimetric analyses under tightly controlled environmental conditions. Mass measurements for both PM_{2.5} and PM₁₀ were obtained between January 31, 2005 and February 6, 2005, and compositional measurements of PM_{2.5} (sulfate, nitrate, ammonium, organic carbon, elemental carbon, phosphate, chloride, sodium, and potassium) were obtained for 3 February, 2005 which was the peak day at the majority of urban areas in the Midwest. Table S1 provides more information about which PM_{2.5}, PM₁₀, and CSN monitoring sites we chose to use, and justifications for the selection of each site.

RESULTS AND DISCUSSION

The goal of this study was to arrive at a scientific understanding of the main components of PM_{2.5} during winter elevated PM episodes in the Midwest, and thereby gain insight into the source contributions of these components. This study is intended to help State agencies

Table 3. EPA PM_{2.5} Mass measurements made at 18 cities in the area of the Midwest affected by the PM episode. All of the cities selected were part of Metropolitan Statistical Areas (MSA; defined by the US Census Bureau) with populations in excess of one million people. Exceptions were Toledo and Akron, OH, Gary, IN, and Green Bay, WI which are included because they are industrial centers, and Des Moines since it was the largest MSA in Iowa. The cities are organized from west to east. For cities with multiple sampling sites, the site chosen was the highest frequency monitoring site located closest to the urban center (Table S1). The concentrations in bold exceeded the PM National Ambient Air Quality Standards.

City	Latitude (°N)	Longitude (°W)	Annual Average (μg/m ³) ^a	24-hour average concentration (μg/m ³) ^b						
				31 Jan. 05	1 Feb. 05	2 Feb. 05	3 Feb. 05	4 Feb. 05	5 Feb. 05	6 Feb. 05
Kansas City, MO	39.10	94.57	14.1	32.6	30.4	36.2	32.7	13.0	12.7	15.0
Des Moines, IA	41.60	93.64	11.3	47.0	45.9	44.0	25.2	9.3	11.5	11.5
Minneapolis, MN	44.95	93.25	10.3	56.3	§	§	16.5	§	§	8.0
St. Paul, MN	44.90	93.02	12.2	69.9	§	§	19.8	§	§	11.0
St. Louis, MO	38.54	90.26	15.9	46.9	41.6	48.3	38.1	27.8	21.0	§
Green Bay, WI	44.52	87.99	11.7	26.1	§	§	41.5	§	§	33.2
Milwaukee, WI	43.04	87.92	14.4	37.1	§	§	43.6	§	§	31.5
Chicago, IL	41.97	87.75	17.0	§	28.9	52.0	62.6	61.5	39.5	28.7
Gary, IN	41.57	87.41	18.7	49.7	§	§	38.8	§	§	33.3
Muskegon, MI	43.23	86.24	13.1	24.8	§	§	48.7	§	§	36.5
Indianapolis, IN	39.74	86.17	19.1	63.2	§	§	43.3	§	§	16.7
Louisville, KY	39.19	85.78	16.5	21.8	31.2	31.4	38.5	29.9	19.3	14.0
Cincinnati, OH	39.28	84.37	16.6	46.6	§	§	41.0	§	§	16.7
Toledo, OH	41.64	83.55	15.8	31.0	§	§	46.0	§	§	45.3
Detroit, MI	42.36	83.10	16.0	38.2	52.5	51.8	75.8	75.0	79.0	46.4
Columbus, OH	40.00	82.99	16.4	46.2	§	§	45.0	§	§	27.6
Cleveland, OH	41.48	81.68	19.2	42.2	§	§	43.2	§	§	43.1
Akron, OH	41.06	81.47	16.4	31.2	§	§	43.6	§	§	30.1

Source: US EPA, 2008; § Data not available for this day at site studied; ^a Annual PM_{2.5} NAAQS was 15 μg/m³; ^b 2006 revision of 24-hour PM_{2.5} NAAQS (35 μg/m³) was used for future planning purposes, although the 1997 24-hour PM NAAQS (65 μg/m³) was still in use at time of study.

tasked with reversing current and future non-attainment designations for $\text{PM}_{2.5}$ in the Midwest. The analyses presented here are different than those used by the EPA (described in the introduction) to determine whether or not sample collection sites are in attainment of the NAAQS, and are not intended to be used in regulatory judgments. Our analyses are intended to highlight the seasons during which concentrations greater than the 24-hour and annual NAAQS were measured, to allow air quality managers to observe directly which months of year were typically the most likely to be contributing to non-attainment designations. To achieve this we compared several years of individual day $\text{PM}_{2.5}$ concentrations directly to both the 24-hour and annual NAAQS on a day-by-day, and monthly averaged basis (Table 1 and Fig. 1).

The EPA archive (2000–2007) of Federal Reference Methods $\text{PM}_{2.5}$ mass concentrations demonstrated that elevated PM concentration episodes in excess of the $\text{PM}_{2.5}$ 24-hour NAAQS (taken as $35 \mu\text{g}/\text{m}^3$ for the reasons discussed in the introduction) were typically more frequent during winter months in the northern cities and more frequent during the summer in the southern cities of the study region (Figs. 1a & b; Table 1). Comparison of the daily average concentrations against the annual NAAQS gives an idea of which season would be more likely to contribute to non-attainment of the annual average in the cities studied. Excesses followed a similar pattern as excesses of the 24-hour NAAQS, although differences in the percentages of excesses between winter and summer were much smaller. The greater number of winter PM

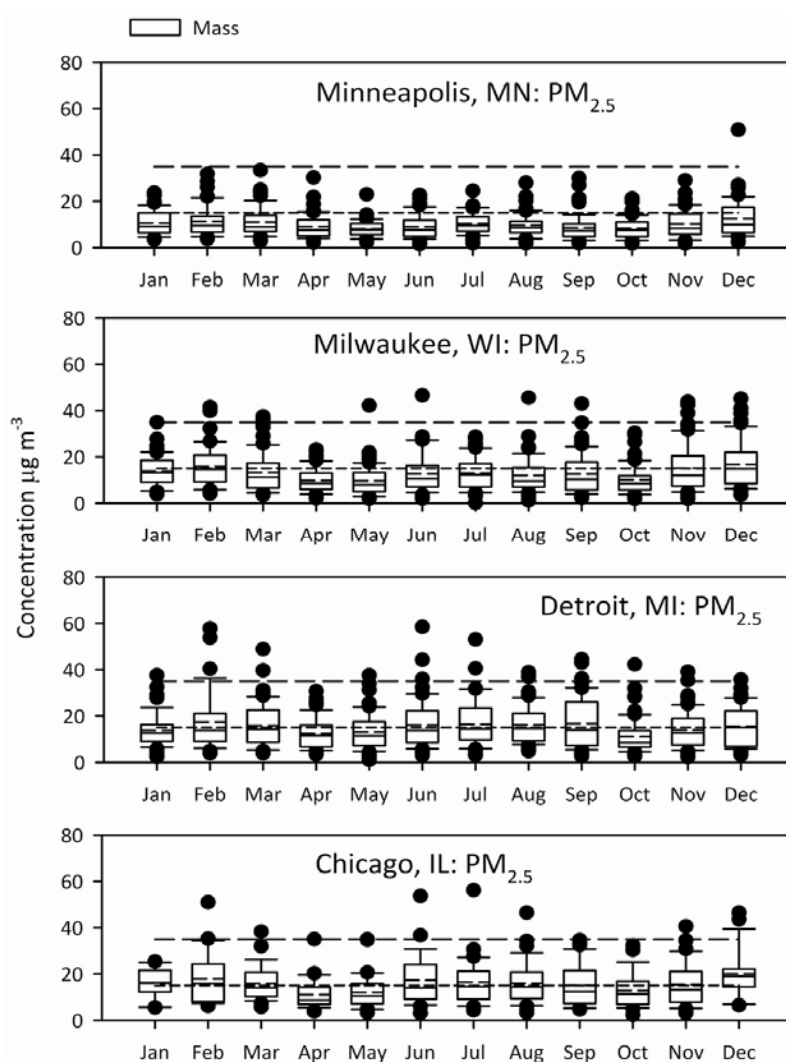


Fig. 1a & b. Measurements of $\text{PM}_{2.5}$ mass made by the EPA, using the Criteria Pollutant Monitoring network. Measurements shown were made at: (a) Minneapolis, MN, Milwaukee, WI, Detroit, MI and Chicago, IL, and; (b) Cleveland, OH; Indianapolis, IN; Cincinnati, OH, and; Saint Louis, MO. Measurements were made during the dates shown in Table 3 (typically 2000–2007). The box plots show the 10th and 90th percentiles as whiskers, the 25th and 75th percentiles as the box ends, the median as a solid line intersecting the box, the mean as a dashed line, and the data beyond the 10th and 90th percentiles as individual measurements. Annual and 24-hour $\text{PM}_{2.5}$ NAAQS (1997 and 2006, respectively) are shown as dashed lines at $15 \mu\text{g}/\text{m}^3$ and $35 \mu\text{g}/\text{m}^3$ to highlight periods of the year when concentrations in excess of these standards occur to inform air quality strategies. However, these figures are not intended to show whether or not sites are attaining PM NAAQS.

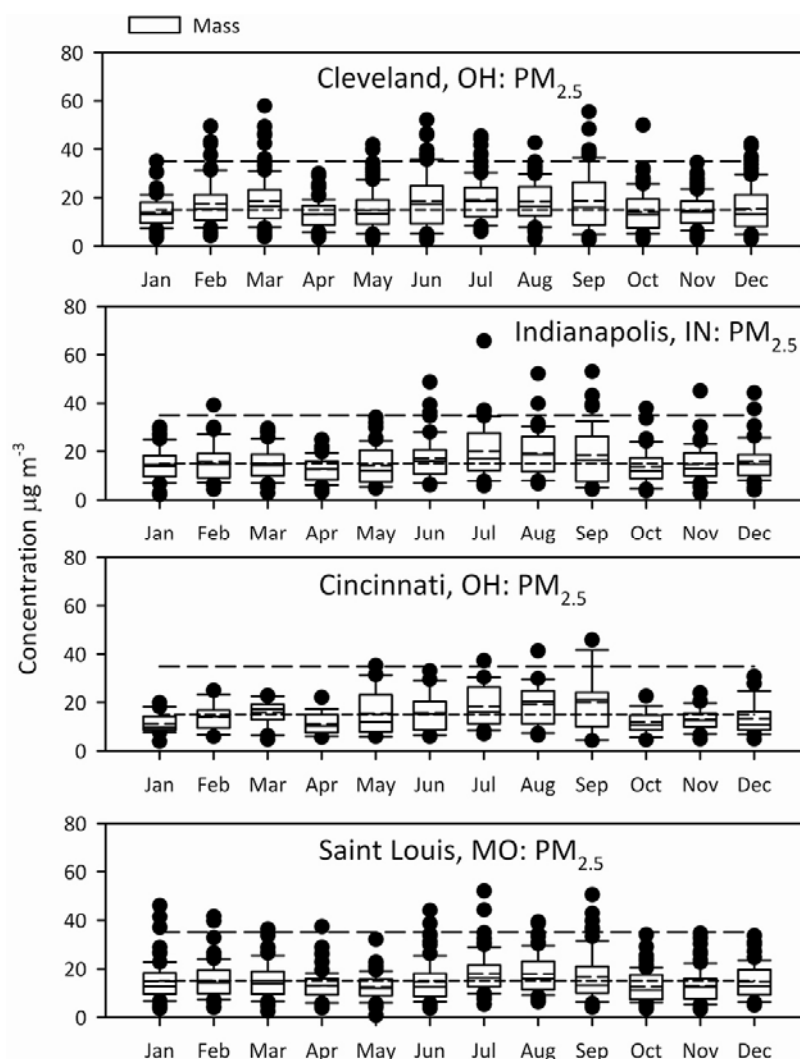


Fig. 1a & b. (continued).

exceedances become more frequent in northerly cities as would be expected given the lower average temperatures, shorter summers, and lower irradiance levels compared with the southerly cities. The temporal, seasonal, and episodic behavior of PM at Milwaukee was expected given the regional spatial and seasonal patterns of PM concentrations and compositions. In this way PM measurements made at Milwaukee corroborated the spatial trends, seasonal trends, and annual averages in $PM_{2.5}$ concentrations and compositions seen in other cities in the study area and therefore was considered broadly representative of the air quality in the region. Figs. S1–S8 revealed that nitrate was the single largest component driving the winter exceedances, whereas summer exceedances were more associated with sulfate and organic carbon. The characteristics revealed in Figs. 1 and Figs. S1–S8 demonstrated that the study cities behaved similarly to locations previously examined in the published literature during both elevated PM episodes and during other times of the year (Tolocka *et al.*, 2001; Chu, 2004; Malm *et al.*, 2004; Fischer and Talbot, 2005; Kim and Hopke, 2005; Bell *et al.*, 2007; Bell *et al.*, 2008; Zhou *et al.*, 2009).

Chemical composition measurements of $PM_{2.5}$ and PM_{10} were made in Milwaukee, WI on a 1-in-6 schedule between 2004–2005 (Figs. 2a and 2b). In order to improve the readability of the compositional information, 1-in-6 day measurements have been presented next to each other; days on which no measurements were made have been omitted from the figure. Several elevated concentration episodes were observed during winter months, most of which were in the same range of measurements made in other years (Fig. S2). During the February 2005 PM episode a maximum daily average concentration of $43.6 \mu g m^{-3}$ was recorded by the EPA Federal Reference Method, which was among the highest concentrations previously reported at Milwaukee, WI. The bulk composition of $PM_{2.5}$ measured by UW-Madison demonstrated that nitrate disproportionately contributed to the elevated concentrations during the episode (30% vs 10–15% winter average). This same characteristic was observed during other late fall and winter PM episodes which were elevated over the 99% confidence limit of the annual average (mean + 99% C.L. = $11.5 + 3.4$; episode dates = November 17, 2004, December 29, 2004, March 5 and 29, 2005). This similarity between winter episodes

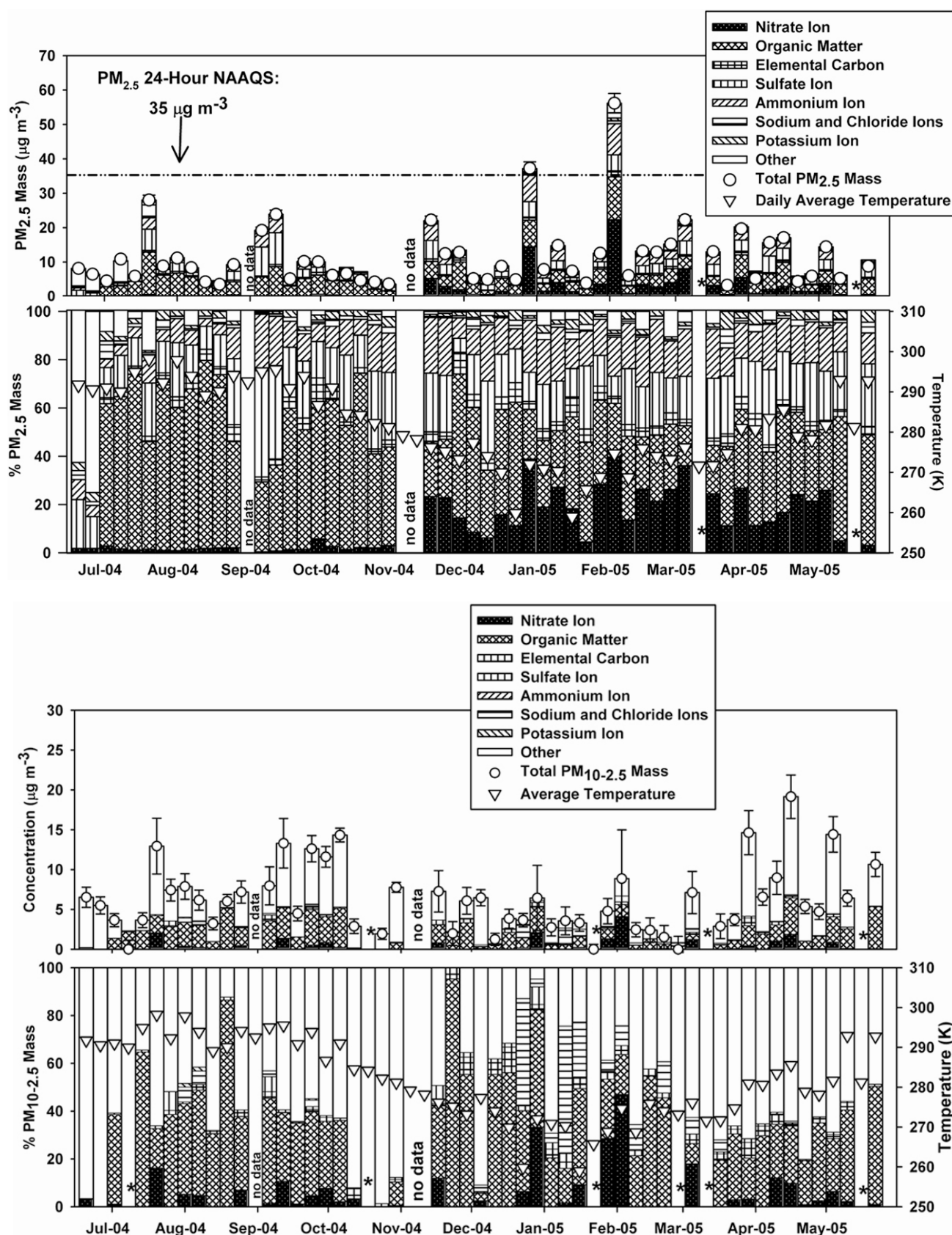


Fig. 2a & b. Absolute and relative bulk chemical composition of $PM_{2.5}$ (a) and $PM_{10-2.5}$ (b) mass measured at Milwaukee, WI between June 2004 and June 2005 (a). Also included is the daily average temperature. The symbol * denotes that mass measurements and reconstructions of mass from chemical composition data conducted by UW-Madison were significantly different for these days. Therefore the data was omitted.

demonstrated that the $PM_{2.5}$ composition during the February 2005 PM episode was representative of other winter PM episodes in Milwaukee during 2005. Temperatures recorded during the high PM episodes were all either similar, or slightly warmer, than the preceding and proceeding measurement days, confirming that the observed increases in particulate nitrate could not be explained by a shift in gas to particle partitioning of existing ammonium nitrate due to decreases in ambient temperature (Yu *et al.*, 2006; Fountoukis *et al.*, 2009). Furthermore, changes in relative humidity during the February 2005 episode could not explain the enrichment in particulate nitrate either ((USEPA, 2008), data not shown; (Seinfeld and Pandis, 1998)). Enrichments in particulate nitrate observed during the February 2005 episode, during which a regional stagnation in meteorology occurred as described in the introduction (LADCO, 2009), were consistent with a reduced ventilation rate of the urban air space. This increased the residence time of PM precursors in the urban air space, and allowed more than typical in-situ production of nitric acid and ammonium nitrate from local sources of NO_x and NH_3 . After formation the newly produced nitric acid and ammonium nitrate would then thermodynamically partition between the gas and particle phases. Under normal ventilation rates and associated residence times this formation would have occurred downwind of the urban area, and have been diluted during dispersion.

Concentrations of particulate matter sized between $2.5\ \mu m$ and $10\ \mu m$ (hereafter $PM_{10-2.5}$; also referred to as “coarse PM” and “thoracic PM”) increased during the winter

elevated PM concentration episodes at Milwaukee (Fig. 2b). The year-long concentration time series of $PM_{10-2.5}$ demonstrated that $PM_{10-2.5}$ differed during the episode periods with disproportionately large contributions from nitrate (30–50%). However, elevated $PM_{10-2.5}$ concentrations did not always correspond to elevated $PM_{2.5}$ concentrations during all seasons; the February 2005 episode was not the $PM_{10-2.5}$ concentration maximum during the study, this occurring in the spring, on April 16, 2005. Elevated $PM_{10-2.5}$ concentration episodes were observed in summer, fall and spring, apparently driven by the “other” category, believed to be crustal in nature.

Temporal and spatial examination of the February 2005 PM episode revealed that it developed from west to east across the region (Fig. 3). The three panels divided the selected cities from the Midwest between western, central and eastern geographical regions. The city locations and results presented in Fig. 3 are also presented as a map in Fig. S12 of the supplemental materials. Most of the cities chosen to be included in our regional examination of the episode all had Metropolitan Statistical Areas (MSAs; defined by the US Census Bureau) with populations exceeding one million people, with the exceptions of Gary, IN, Green Bay, WI, Akron, OH and Toledo, OH. These cities were included due the disproportionately large amount of heavy industry located there. Since none of the MSAs in Iowa exceeded one million people, the largest MSA, Des Moines, was used to represent the state. For cities with multiple samplers, the data presented was from the 1-in-3 day, or daily sampler nearest the city’s urban

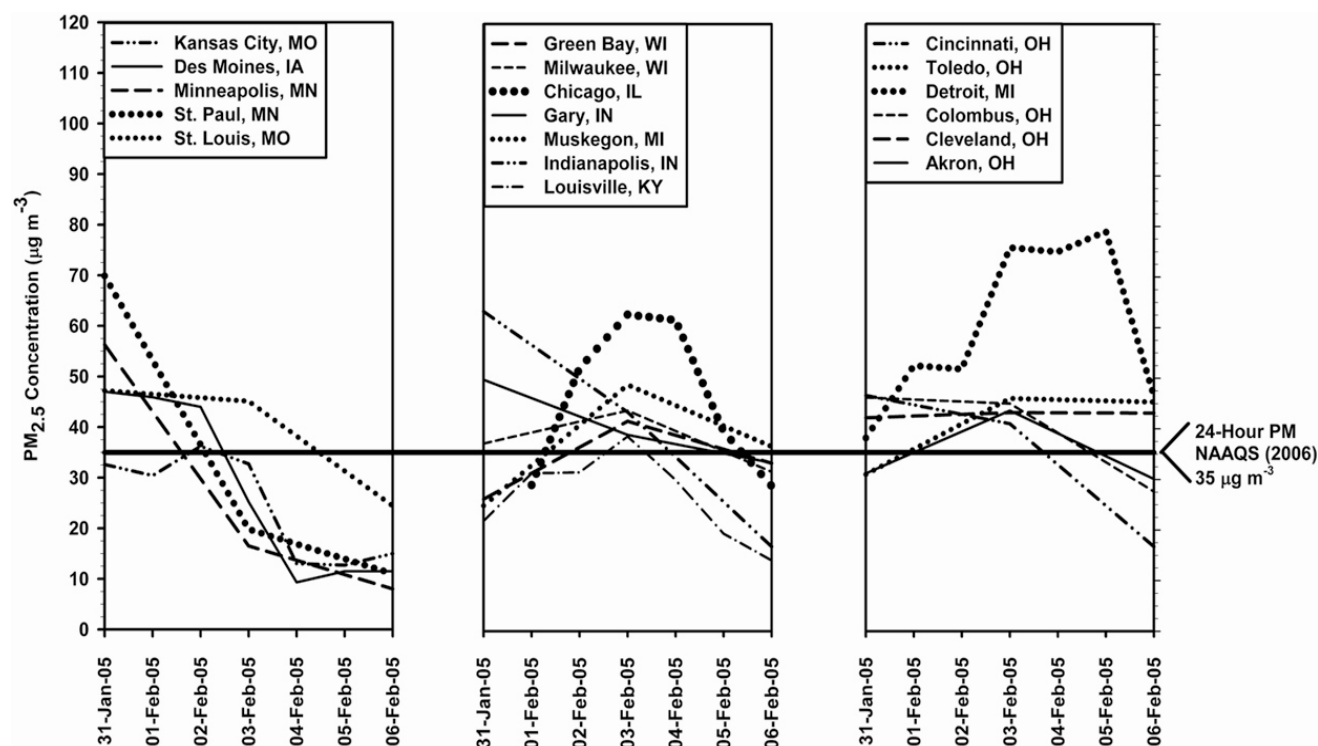


Fig. 3. A comparison of the $PM_{2.5}$ mass concentrations made during the February 2005 PM episode across the major cities in the Midwest. The cities were divided geographically into western (left panel), central (middle panel) and eastern regions (right panel). Consequently, the figure illustrates the progression of the episode from west (far left) to east (far right).

center (see Table S1). An exception to this protocol was made for Saint Louis, where the PM sampler colocated with the CSN site was selected, despite not being the closest to downtown, or having the highest sampling frequency in the urban center. All three panels illustrated that PM concentrations exceeded the 2006 24-hour NAAQS ($35 \mu\text{g}/\text{m}^3$) at every location on the day of local peak concentration, and were substantially elevated when compared to the annual averages (Table 3). The west panel clearly showed the episode to have peaked on or before February 2nd, 2005 whereas the central and east panel illustrated that the episode peaked in these areas on February 3rd, 2005. For example, at St Paul, MN the $\text{PM}_{2.5}$ concentration on January 31, 2005 was $69.9 \mu\text{g}/\text{m}^3$ before falling to $19.8 \mu\text{g}/\text{m}^3$ on February 3, and $11 \mu\text{g}/\text{m}^3$ on February 6, which was just below the annual average for the city. In contrast, at Detroit, MI the $\text{PM}_{2.5}$ concentration on January 31st was elevated ($38.2 \mu\text{g}/\text{m}^3$) compared to the annual average of $16.0 \mu\text{g}/\text{m}^3$, but concentrations did not peak until February 5th, at least six days later than St. Paul, MN at $79.0 \mu\text{g}/\text{m}^3$. The evolution of the episode in mass measurements from west to east illustrated this episode was driven by mesoscale to synoptic scale meteorology and that the elevated concentrations measured across the entire Midwest were connected and not coincidental.

At Milwaukee, the peak day of the episode occurred on February 3, 2005. Daily measurements of PM composition

were made in addition to the 1-in-6 day collections during the week of the episode at Milwaukee, WI (January 31–February 6, 2005; Fig. 4). This additional data, which was not presented in Fig. 2, allowed a more highly time resolved observation of how the particle constituents changed throughout the growth and subsequent decay in mass concentrations. The composition of the $\text{PM}_{2.5}$ mass was significantly different during the high PM episode compared to compositions typical of baseline concentration days (Fig. 2a) and the annual average (Fig. 4). It was apparent that total $\text{PM}_{2.5}$ mass and nitrate concentrations increased during the episode (mass increased from $12.5 \mu\text{g}/\text{m}^3$ on Jan 28, to $56.1 \mu\text{g}/\text{m}^3$ on February 3, before falling back to $33 \mu\text{g}/\text{m}^3$ on February 4) and were higher than other periods of the winter and the rest of the year. The relative increase in nitrate concentration contrasted with relative decreases in the concentrations of organic matter ($\text{OM}/\text{OC} = 1.7$ after (Polidori *et al.*, 2008) who stated current literature indicated 1.6–1.8 to be reasonable for urban aerosol) and sulfate (a small portion of the total mass) between the episode and non-episode periods. This may have been due to competition between the different secondary processes for oxidants (Tsimpidi *et al.*, 2008). The daily sample collections and analyses made during the episode (Fig. 4) clearly demonstrated that nitrate was the main cause of the exceedance of the $\text{PM}_{2.5}$ 24-hour NAAQS. High time resolved measurements of $\text{PM}_{10-2.5}$ composition in

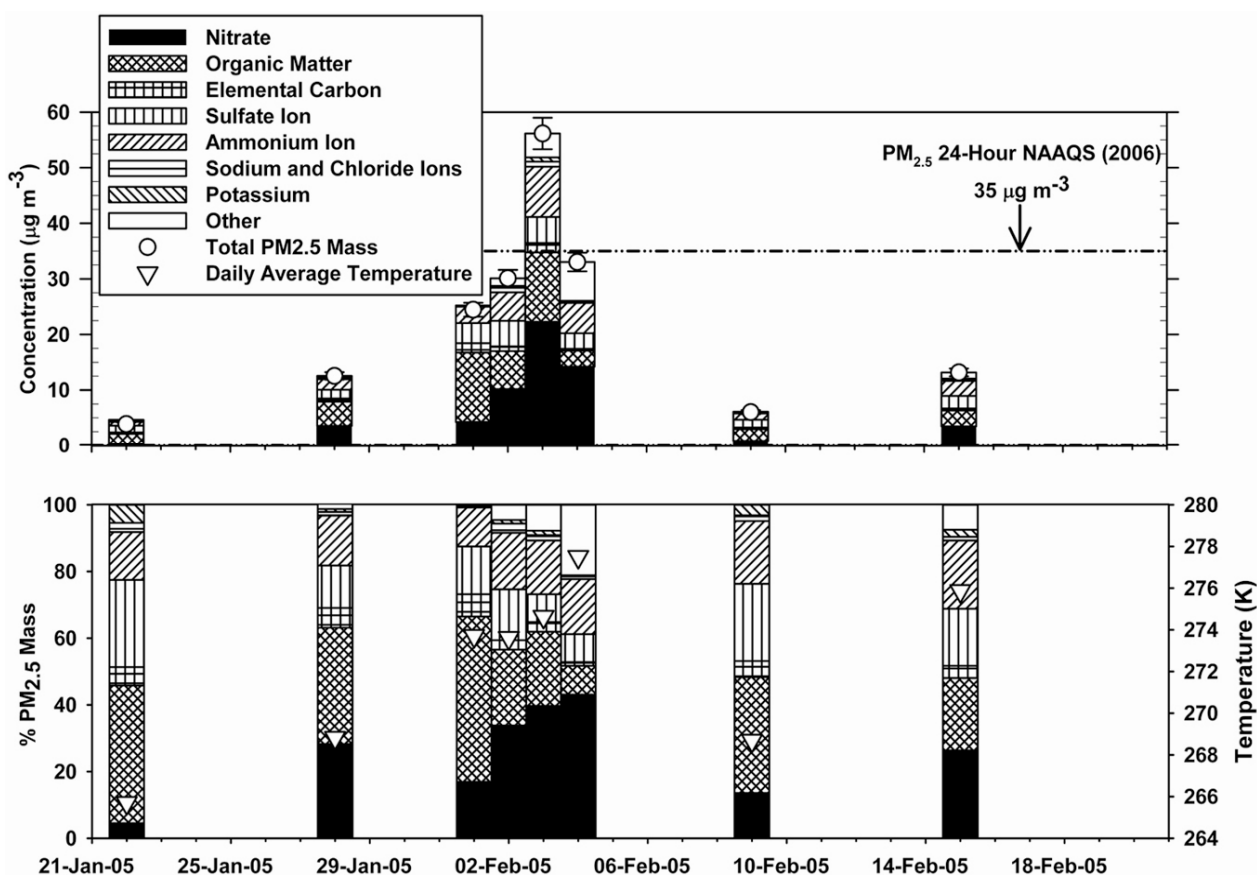


Fig. 4. Absolute and relative bulk chemical compositions for $\text{PM}_{2.5}$ made between 22 January and 15 February, 2005 by UW-Madison.

Milwaukee during the February 2005 PM episode (Fig. S13) also showed that nitrate increased to a maximum on February 3 and was the single largest component on that day.

Fig. 5 presents PM composition for the cities in the study region during the February, 2005 episode and throughout the year as an annual average. The cities are arranged in the figure with respect to latitude inside of 3 sections for western, central and eastern cities in the study region. The composition of PM_{2.5} during the peak day for the majority of cities in the study area, February 3rd, 2005 exhibited a north-south gradient in nitrate, organic carbon, and total mass concentrations (Fig. 5a). In contrast, contributions of sulfate showed an inverse gradient, decreasing with increasing latitude (Fig. 5a). Temperature data from the Chemical Speciation Network revealed that the increase in total PM_{2.5} concentrations with latitude did not correlate with the trend in average temperatures which reached a minimum in the middle of the study of area, rather than the extreme north on February 3, 2005. The reason for increasing absolute and relative concentrations in nitrate and organic carbon, and decreasing concentrations of sulfate was not discernible from the data available, and would require interpretation with an urban air quality model such as PMCAMx (Tsimpidi, *et al.*, 2008).

Fig. 5 did not include data for Saint Louis, Saint Paul, and Minneapolis, because peak concentrations did not occur on February 3, 2005. Muskegon, MI and Green Bay, WI were not included because the EPA Chemical Speciation Network did not monitor at these locations.

Measurements of NO₂ made by the EPA criteria pollutants monitoring network are used to protect human health, but might also be attractive to some agencies as an ad-hoc metric related to NO_x and NO_y, precursors to PM_{2.5} nitrate. Measurements of NO₂ from demonstrated that all of the locations were in attainment of the NO₂ NAAQS, and therefore the standard is unlikely to be useful in preventing winter time PM_{2.5} NAAQS exceedances in its current form.

CONCLUSIONS

High wintertime PM_{2.5} mass concentrations at northern cities in the Midwest were shown to be more frequent than summertime episodes, and vice versa for cities south of the Great Lakes. This finding demonstrated that air quality management strategies in such cities may need to consider mitigation strategies that emphasize either winter or summer, or both seasons, for future attainment of PM NAAQS depending on how far north or south in the study domain they are located. All of the data presented in this study demonstrated that wintertime elevated PM episodes were driven by nitrate, assumed to be present as ammonium nitrate and nitric acid, while summer time episodes were driven by OC and sulfate. This means that different strategies will need to be pursued depending on which season and therefore component causes the majority of NAAQS excesses in a given city. This study also demonstrated that nitric acid and ammonium nitrate contributed to high wintertime concentrations of PM_{10-2.5}

in Milwaukee, WI. This finding indicated that controls aimed at reducing PM_{2.5} nitrate concentrations during winter stagnations would also help mitigate PM_{10-2.5} concentrations, should the need arise in future regulatory climates.

The wintertime excesses driven by nitrate could have been caused by several factors: i) decreased ventilation rates of urban air spaces due to various scales of meteorological stagnation; ii) emissions of the nitrate precursor NO_x from combustion sources associated with urban areas, such as motor vehicles and stationary sources into the stagnant air mass (Schauer, 1998; Schauer *et al.*, 1999; Schauer *et al.*, 1999; Schauer and Cass, 2000; Schauer *et al.*, 2001; Schauer *et al.*, 2002; Bae *et al.*, 2006; Brown *et al.*, 2007); iii) cold temperatures typical of high latitude cities during winter, which enhanced the partitioning of nitric acid and ammonium nitrate to PM; and, iv) increases in relative humidity sufficient to cause deliquescence and associated increases in particulate nitrate. Temperature measurements made during the February 2005 elevated PM episode excluded the possibility that the temporary excesses above the 24-hour NAAQS observed at Milwaukee were driven solely by thermodynamic shifts in gas-to-particle partitioning of nitric acid and ammonium nitrate. Therefore other aspects of meteorology and source emissions were thought to be the most important contributing factors in the February 2005 PM episode. However, model simulations would need to be conducted to confirm this hypothesis.

The most obvious strategy to reduce wintertime particulate nitrate at first inspection appears to be the reduction of NO_x. However, Blanchard and Tanenbaum, 2008 found that particulate nitrate formation on February 3, 2005 in most of the affected regions was ammonia limited indicating that wintertime PM control strategies need to also consider the importance of agricultural ammonia emissions. Furthermore, Tsimpidi *et al.* (2008) demonstrated with modeling experiments that reducing NO_x emissions alone achieved only insufficient total PM_{2.5} decreases, and in some cases caused increases in PM_{2.5}. This counterintuitive outcome was driven by lower suppression of gas phase oxidants caused by decreased NO_x concentrations following emission reductions. The higher oxidant levels in turn led to increases oxidation of sulfur dioxide gas (SO₂) and volatile organic carbon compounds (VOCs) producing additional secondary sulfate and secondary organic carbon in PM_{2.5}, thereby compensating for intended reductions in particulate nitrate. Therefore, any mitigation strategy aimed at eradicating winter exceedances of the 24-hour PM_{2.5} NAAQS in any of the cities studied would need to consider simultaneous reductions in NO_x, NH₃, SO₂ and VOCs and be evaluated with model simulations (LADCO, 2009; Tsimpidi *et al.*, 2008).

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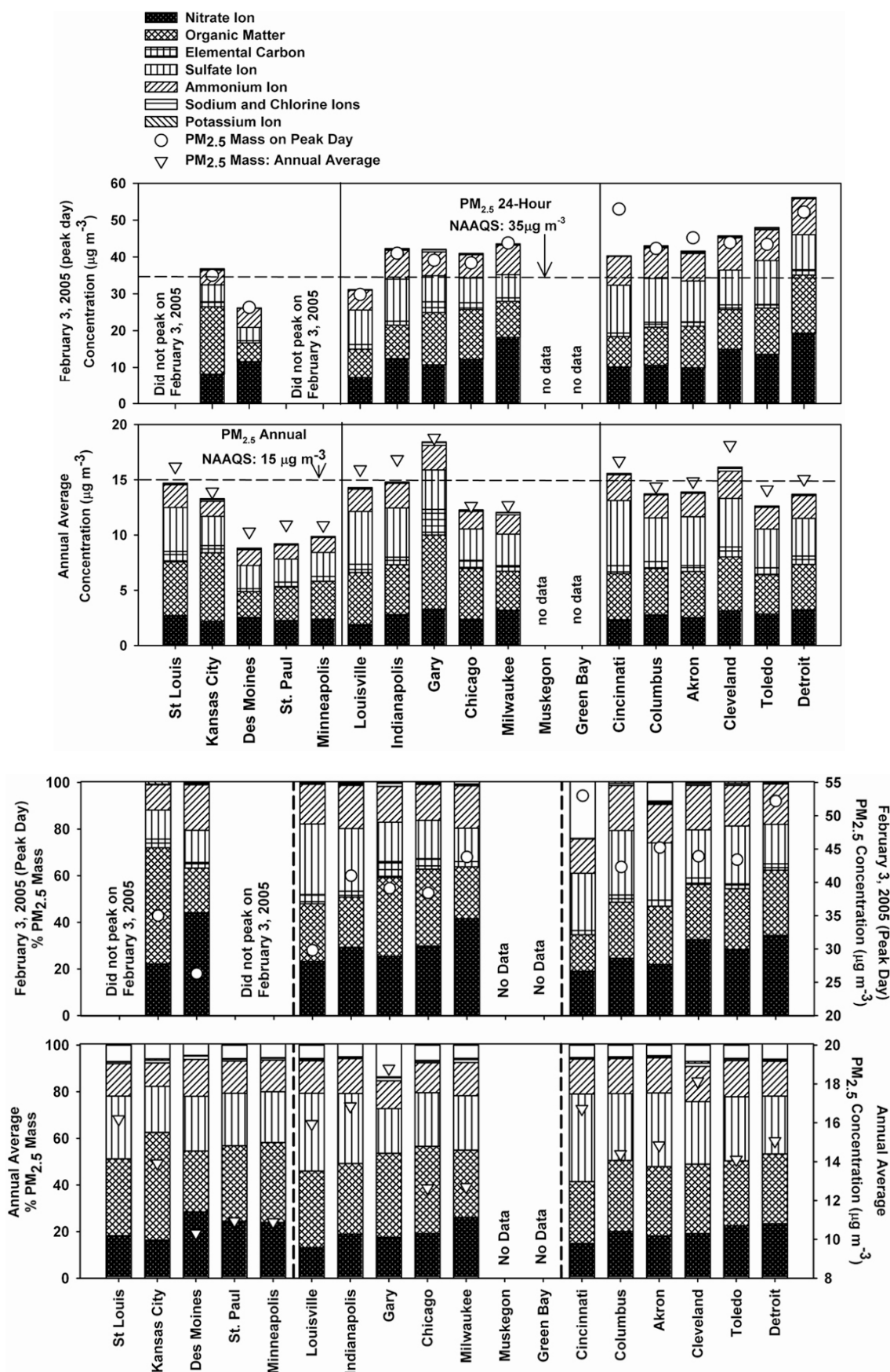


Fig. 5a & b. PM_{2.5} composition from the EPA Chemical Speciation Network on February 3, 2005, which was the peak day of the February, 2005 PM episode at the majority of the Midwestern cities examined in this study, including Milwaukee, WI.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

REFERENCES

- Bae, M.S., Schauer, J.J. and Turner, J.R. (2006). Estimation of the Monthly Average Ratios of Organic Mass to Organic Carbon for Fine Particulate Matter at an Urban Site. *Aerosol Sci. Technol.* 40: 1123–1139.
- Bai, N., Khazaei, M., van Eedenc, S.F. and Laher, I. (2007). The Pharmacology of Particulate Matter Air Pollution-induced Cardiovascular Dysfunction. *Pharmacol. Ther.* 113: 16–29.
- Bell, M.L., Dominici, F., Ebisu, K., Zeger, S.L. and Samet, J.M. (2007). Spatial and Temporal Variation in PM_{2.5} Chemical Composition in the United States for Health Effects Studies. *Environ. Health Perspect.* 115: 989–995.
- Bell, M. L., Ebisu, K., Peng, R.D., Samet, J.M. and Dominici, F. (2009). Hospital Admissions and Chemical Composition of Fine Particle Air Pollution. *Am. J. Respir. Crit. Care Med.* 179: 1115–1120.
- Bell, M.L., Ebisu, K., Peng, R.D., Walker, J., Samet, J.M., Zeger, S.L. and Dominici, F. (2008). Seasonal and Regional Short-term Effects of Fine Particles on Hospital Admissions in 202 US Counties, 1999–2005. *Am. J. Epidemiol.* 168: 1301–1310.
- Blanchard, C.L. and Tanenbaum, S. (2008). Analysis of Inorganic Particulate Matter Formation in the Midwestern United States. http://www.ladco.org/reports/rpo/data_analysis/analysis_of_midwest_ammonia_data.pdf, Lake Michigan Air Directors Consortium, Rosemont, IL.
- Brown, S.G., Hafner, H.H. Roberts, P.T., Sheesley, R.J. and Schauer, J.J. (2007). Integration of Results for the Upper Midwest Organics Study; STI-903520-2942-FR. Retrieved 18 July, 2007, 2007, from www.ladco.org/reports/rpo/MWRPOprojects/Monitoring/Integration_FinalReport.pdf.
- Brunekreef, B. and Forsberg, B. (2005). Epidemiological Evidence of Effects of Coarse Airborne Particles on Health. *Eur. Respir. J.* 26: 309–318.
- Chu, S.H. (2004). PM_{2.5} Episodes as Observed in the Speciation Trends Network. *Atmos. Environ.* 38: 5237–5246.
- Dockery, D.W., Pope, C.A. Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G. and Speizer, F.E. (1993). An Association between Air-Pollution and Mortality in 6 United-States Cities. *New Engl. J. Med.* 329: 1753–1759.
- Fischer, E. and Talbot, R. (2005). Regional NO₃⁻ Events in the Northeastern United States Related to Seasonal Climate Anomalies. *Geophys. Res. Lett.* 32: L16804.
- Fountoukis, C., Nenes, A., Sullivan, A., Weber, R., van Reken, T., Fischer, M., Matías, E., Moya, M., Farmer, D. and Cohen, R.C. (2009). Thermodynamic Characterization of Mexico City Aerosol during MILAGRO 2006. *Atmos. Chem. Phys.* 9: 2141–2156.
- Franklin, M., Koutrakis, P. and Schwartz, P. (2008). The Role of Particle Composition on the Association between PM_{2.5} and Mortality. *Epidemiology.* 19: 680–689.
- Fraser, M.P., Kleeman, M.J. Schauer, J.J. and Cass, G.R. (2000). Modeling the Atmospheric Concentrations of Individual Gas-Phase and Particle-Phase Organic Compounds. *Environ. Sci. Technol.* 34: 1302–1312.
- Kim, E. and Hopke, P.K. (2005). Identification of Fine Particle Sources in Mid-Atlantic US Area. *Water Air Soil Pollut.* 168: 391–421.
- LADCO, (2009). Supplemental Information to Conceptual Model of PM_{2.5} Episodes in the Midwest. http://ladco.org/reports/pm25/post08/pm2.5_conceptual_model.pdf. Lake Michigan Air Directors Consortium, Rosemont, IL.
- Lauer, F.T., Mitchell, L.A., Bedrick, E., McDonald, J.D., Lee, W.Y., Li, W.W., Olvera, H., Amaya, M.A., Berwick, M., Gonzales, M., Currey, R., Pingitore Jr, N.E. and Burchiel, S.W. (2009). Temporal-Spatial Analysis of US-Mexico Border Environmental Fine and Coarse PM Air Sample Extract Activity in Human Bronchial Epithelial Cells. *Toxicol. Appl. Pharmacol.* 238: 1–10.
- Lin, M., Stieb, D.M. and Chen Y. (2005). Coarse Particulate Matter and Hospitalization for Respiratory Infections in Children Younger than 15 Years in Toronto: A Case-Crossover Analysis. *Pediatrics* 116: E235–E240.
- Malm, W.C., Schichtel, B.A., Pitchford, M.L., Ashbaugh, L.L. and Eldred, R.A. (2004). Spatial and Monthly Trends in Speciated Fine Particle Concentration in the United States. *J. Geophys. Res.* 109: D03306.
- Pekney, N.J., Davidson, C.I., Robinson, A., Zhou, L.M., Hopke, P., Eatough, D. and Rogge, W.F. (2006). Major source categories for PM_{2.5} in Pittsburgh using PMF and UNMIX. *Aerosol Sci. Technol.* 40: 910–924.
- Peng, R.D., Bell, M.L., et al. (2009). Emergency Admissions for Cardiovascular and Respiratory Diseases and the Chemical Composition of Fine Particle Air Pollution. *Environ. Health Perspect.* 117: 957–963.
- Peng, R.D., Dominici, F., Pastor-Barriuso, R., Zeger, S.L. and Samet, J.M. (2005). Seasonal Analyses of Air Pollution and Mortality in 100 US Cities. *Am. J. Epidemiol.* 161: 585–594.
- Polidori, A., Turpin, B.J., Davidson, C.I., Rodenburg, L.A. and Maimone, F. (2008). Organic PM_{2.5}: Fractionation by Polarity, FTIR Spectroscopy, and OM/OC Ratio for the Pittsburgh Aerosol. *Aerosol Sci. Technol.* 42: 233–246.
- Pope, C.A. (2000). Epidemiology of Fine Particulate Air Pollution and Human Health: Biologic Mechanisms and Who's at Risk? *Environ. Health Perspect.* 108: 713–723.
- Pope, C.A. (2007). Mortality Effects of Longer Term Exposures to Fine Particulate Air pollution: Review of Recent Epidemiological Evidence. *Inhal. Toxicol.* 19: 33–38.
- Schauer, J.J. (1998). Source Contributions to Atmospheric Organic Compound Concentrations: Emissions

- Measurement and Model Predictions, Ph.D. dissertation thesis, California Institute of Technology, Pasadena, CA.
- Schauer, J.J. and Cass, G.R. (2000). Source Apportionment of Wintertime Gas-Phase and Particle-Phase Air Pollutants Using Organic Compounds as Tracers. *Environ. Sci. Technol.* 34: 1821–1832.
- Schauer, J.J., Fraser, M.P., Cass, G.R. and Simoneit, B.R.T. (2001). Source Reconciliation of Atmospheric Gas-Phase and Particle-Phase Pollutants Using Organic Compounds as Tracers. *Environ. Sci. Technol.* 36: 3806–3814.
- Schauer, J.J., Fraser, M.P., Cass, G.R. and Simoneit, B.R.T. (2002). Source Reconciliation of Atmospheric Gas-Phase and Particle-Phase Pollutants during a Severe Photochemical Smog Episode. *Environ. Sci. Technol.* 36: 3806–3814.
- Schauer, J.J., Kleeman, M.J., Cass, G.R. and Simoneit, B.R.T. (1999). Measurement of Emissions from Air Pollution Sources. 1. C₁ through C₂₉ Organic Compounds from Meat Charbroiling. *Environ. Sci. Technol.* 33: 1566–1577.
- Schauer, J.J., Kleeman, M.J., Cass, G.R. and Simoneit, B.R.T. (1999). Measurement of Emissions from Air Pollution Sources. 2. C₁ through C₃₀ Organic Compounds from Medium Duty Diesel Trucks. *Environ. Sci. Technol.* 33: 1578–1587.
- Schauer, J.J., Mader, B.T., DeMinter, J. T., Heidemann, G., Bae, M.S., Seinfeld, J.H., Flagan, R.C., Cary, R.A., Smith, D., Huebert, B.J., Bertram, T., Howell, S., Kline, J.T., Quinn, P., Bates, T., Turpin, B., Lim, H.J., Yu, J.Z., Yang, H. and Keywood, M.D. (2003). ACE-Asia Intercomparison of a Thermal-Optical Method for the Determination of Particle-Phase Organic and Elemental Carbon. *Environ. Sci. Technol.* 37: 993–1001.
- Seinfeld, J.H. and Pandis, S.N. (1998). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, Wiley-Interscience, New York.
- Tolocka, M.P., Solomon, P.A., Mitchell, W., Norris, G.A., Gemmill, D.B., Wiener, R.W., Vanderpool, R.W., Homolya, J.B. and Rice, J. (2001). East versus West in the US: Chemical Characteristics of PM_{2.5} during the Winter of 1999. *Aerosol Sci. Technol.* 34: 88–96.
- Tsimpidi, A.P., Karydis, V.A. and Pandis, S.N. (2008). Response of Fine Particulate Matter to Emission Changes of Oxides of Nitrogen and-Anthropogenic Volatile Organic Compounds in the Eastern United States. *J. Air Waste Manage. Assoc.* 58: 1463–1473.
- USEPA (2008). Chemical Speciation Network Database. 2008 (November, 2008).
- USEPA. (2008). Criteria Pollutants Database. Retrieved November, 2008. from <http://www.epa.gov/airexplorer/>.
- Valavanidis, A., Fiotakis, K. and Vlachogianni, T. (2008). Airborne Particulate Matter and Human Health: Toxicological Assessment and Importance of Size and Composition of Particles for Oxidative Damage and Carcinogenic Mechanisms. *J. Environ. Sci. Health., Part C Environ. Carcinog. Ecotoxicol. Rev.* 26: 339–362.
- Williams, R., Case, M., Yeatts, K., Chen, F.L., Scott, J., Svendsen, E., Devlin, R. (2008). Personal Coarse Particulate Matter Exposures in an Adult Cohort. *Atmos. Environ.* 42: 6743–6748.
- Yeatts, K., Svendsen, E., Creason, J., Alexis, N., Herbst, M., Scott, J., Kupper, L., Williams, R., Neas, L., Cascio, W., Devlin, R.B. and Peden, D.B. (2007). Coarse Particulate Matter (PM_{2.5–10}) Affects Heart Rate Variability, Blood Lipids, and Circulating Eosinophils in Adults with Asthma. *Environ. Health Perspect.* 115: 709–714.
- Yu, X.Y., Lee, T.Y., Benjamin, A., Kreidenweis, S.M., Malm, W. and Collett Jr, J. L. (2006). Loss of Fine Particle Ammonium from Denuded Nylon Filters. *Atmos. Environ.* 40: 4797–4807.
- Zanobetti, A. and Schwartz, J. (2009). The Effect of Fine and Coarse Particulate Air Pollution on Mortality: A National Analysis. *Environ. Health Perspect.* 117: 898–903.
- Zhou, L., Hopke, P.K. and Zhao, W. (2009). Source Apportionment of Airborne Particulate Matter for the Speciation Trends Network Site in Cleveland, OH. *J. Air Waste Manage. Assoc.* 59: 321–331.

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Supplemental Information

PM_{2.5} and PM_{10-2.5} Compositions during Wintertime Episodes of Elevated PM Concentrations across the Midwestern USA

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Table S1. Monitors selected for use in this study from the Criteria Pollutants Monitoring Network (FRM for measuring PM_{2.5} masses), and the Chemical Speciation Network (PM_{2.5} bulk composition). Each selection is accompanied with justifications.

City	Site ID-FRM	Frequency	Reason FRM site was chose	Site ID-CSN	Reason CSN site was chosen
Kansas City, MO	290950034	Daily	Highest frequency sampler nearest the urban center	202090021	Only 1 CSN monitoring site
Des Moines, IA	191530030	Daily	Highest frequency sampler nearest the urban center	191530030	Only 1 CSN monitoring site
Minneapolis, MN	270530963	1-in-3 day	Highest frequency sampler nearest the urban center	270530963	Only 1 CSN monitoring site
St. Paul, MN	271230886	1-in-3 day	1-in-3 day sampler with a collection on 2/3/05 (the cedar st. sampler is also a 1-in-3 day sample closer to the city's center, but is missing data for that day)	271230871	Only 1 CSN monitoring site
St. Louis, MO	295100085	1-in-3 day	Closest to urban center with CSN sampler	295100085	Only 1 CSN monitoring site
Green Bay, WI	550090005	1-in-3 day	1-in-3 day sampler (2 on site-chose POC#1)	N/A	No CSN data available
Milwaukee, WI	550790099	1-in-3 day	Highest frequency sampler nearest the urban center	550790026	Only 1 CSN monitoring site
Chicago, IL	170310052	Daily	Highest frequency sampler IN the city of Chicago and NOT a suburb	170310076	Sampler in city and not suburbs – 1-in-3 day sampler with all ions of interest
Gary, IN	180890026	1-in-3 day	Both FRM samplers near city center – both within a block of each other – chose sampler classified by EPA as “Urban and Center City”	180890022	Sampler in city and not suburbs
Muskegon, MI	261210040	1-in-3 day	Only 1 FRM sampler	N/A	No CSN data available
Indianapolis, IN	180970043	1-in-3 day	Highest frequency sampler nearest the urban center	180970078	Only 1 sampler for CSN with data for full year
Louisville, KY	211110044	Daily	Closest daily sampler to urban center	211110043	Closest to the FRM site chosen
Cincinnati, OH	390610006	1-in-3 day	Closest to urban center; located in a commercial rather than an industrial area	3090610040	Only 1 CSN monitoring site
Toledo, OH	390950024	1-in-3 day	Highest frequency sampler nearest the urban center	390950026	Only 1 CSN monitoring site
Detroit, MI	261630016	Daily	Close to urban center, with CSN samplers	261630001	2 samplers at same site – chose one with all ions of interest – also chose the site with 1-in-3 day samplers instead of 1-in-6 day samplers
Columbus, OH	390490024	1-in-3 day	Both sites equidistant to urban center-chose fairground sampling site	390490081	Only 1 CSN monitoring site
Cleveland, OH	390350038	1-in-3 day	Highest frequency sampler nearest the urban center	390350038	Same site as FRM, same Collection frequency
Akron, OH	391530017	1-in-3 day	Only one sampler available	391530023	Only 1 CSN monitoring site

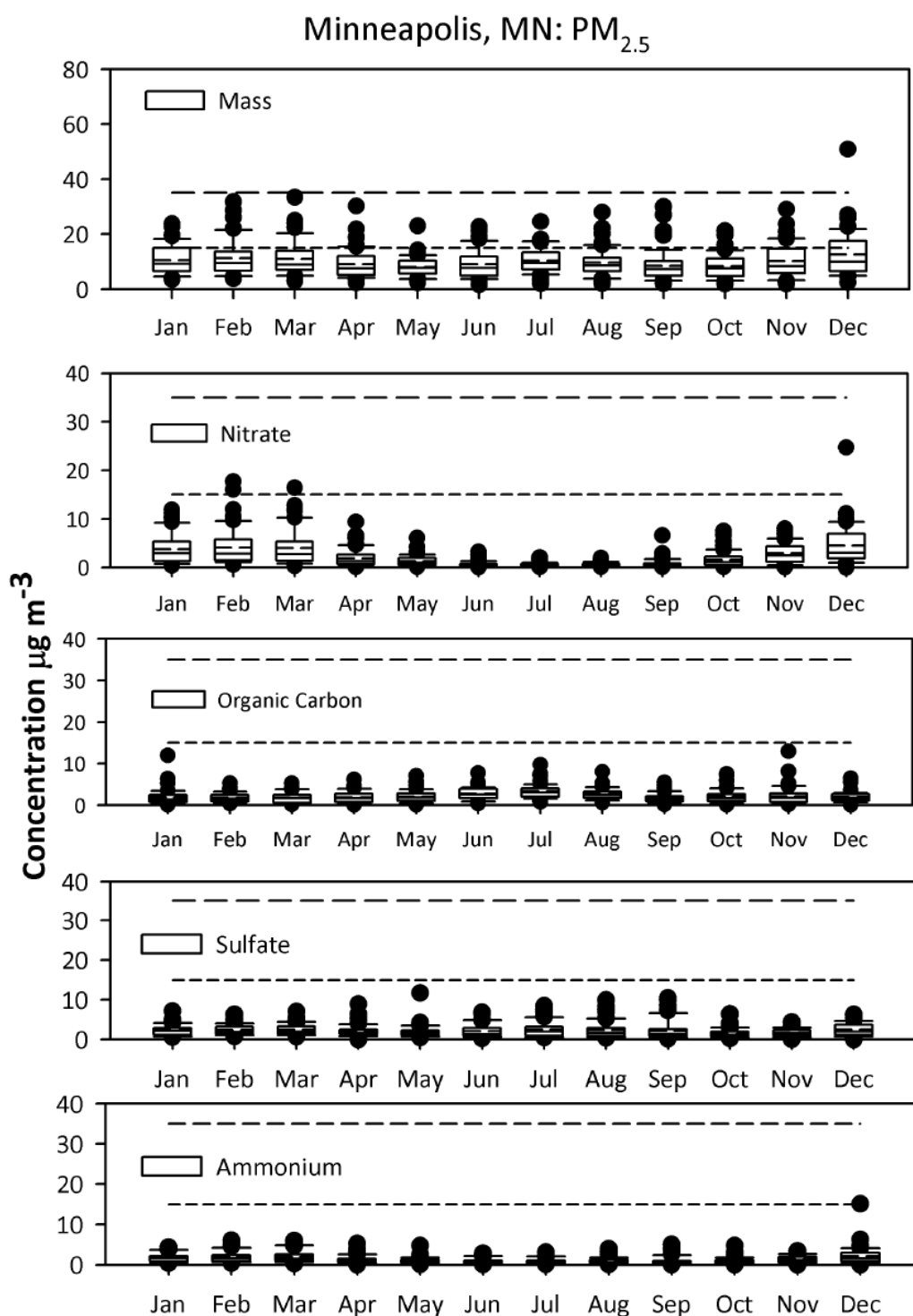


Fig. S1. Measurements of PM_{2.5} mass, nitrate, organic carbon, sulfate and ammonium made at Minneapolis, MN (see Table S1 for sampler numbers, and measurement dates) by the US Environmental Protection Agency using the Criteria Pollutants Network and the Chemical Speciation Network. The box plots show the 10th and 90th percentiles as whiskers, the 25th and 75th percentiles as the box ends, the median as a solid line intersecting the box, the mean as a dashed line, and the data beyond the 10th and 90th percentiles as individual measurements.

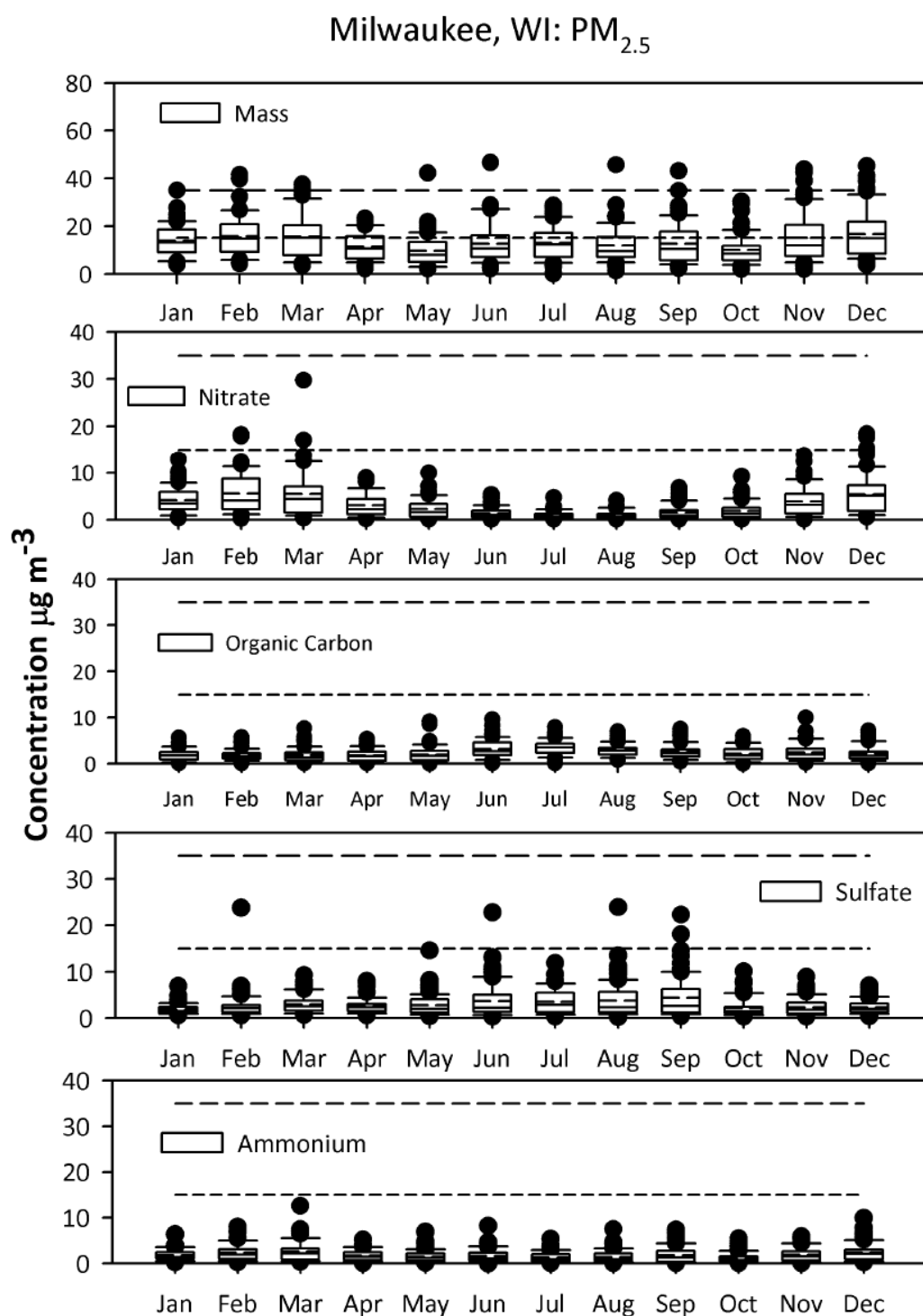


Fig. S2. Measurements of PM_{2.5} mass, nitrate, organic carbon, sulfate and ammonium made at Milwaukee, WI (see Table S1 for sampler numbers, and measurement dates) by the US Environmental Protection Agency using the Criteria Pollutants Network and the Chemical Speciation Network. The box plots show the 10th and 90th percentiles as whiskers, the 25th and 75th percentiles as the box ends, the median as a solid line intersecting the box, the mean as a dashed line, and the data beyond the 10th and 90th percentiles as individual measurements.

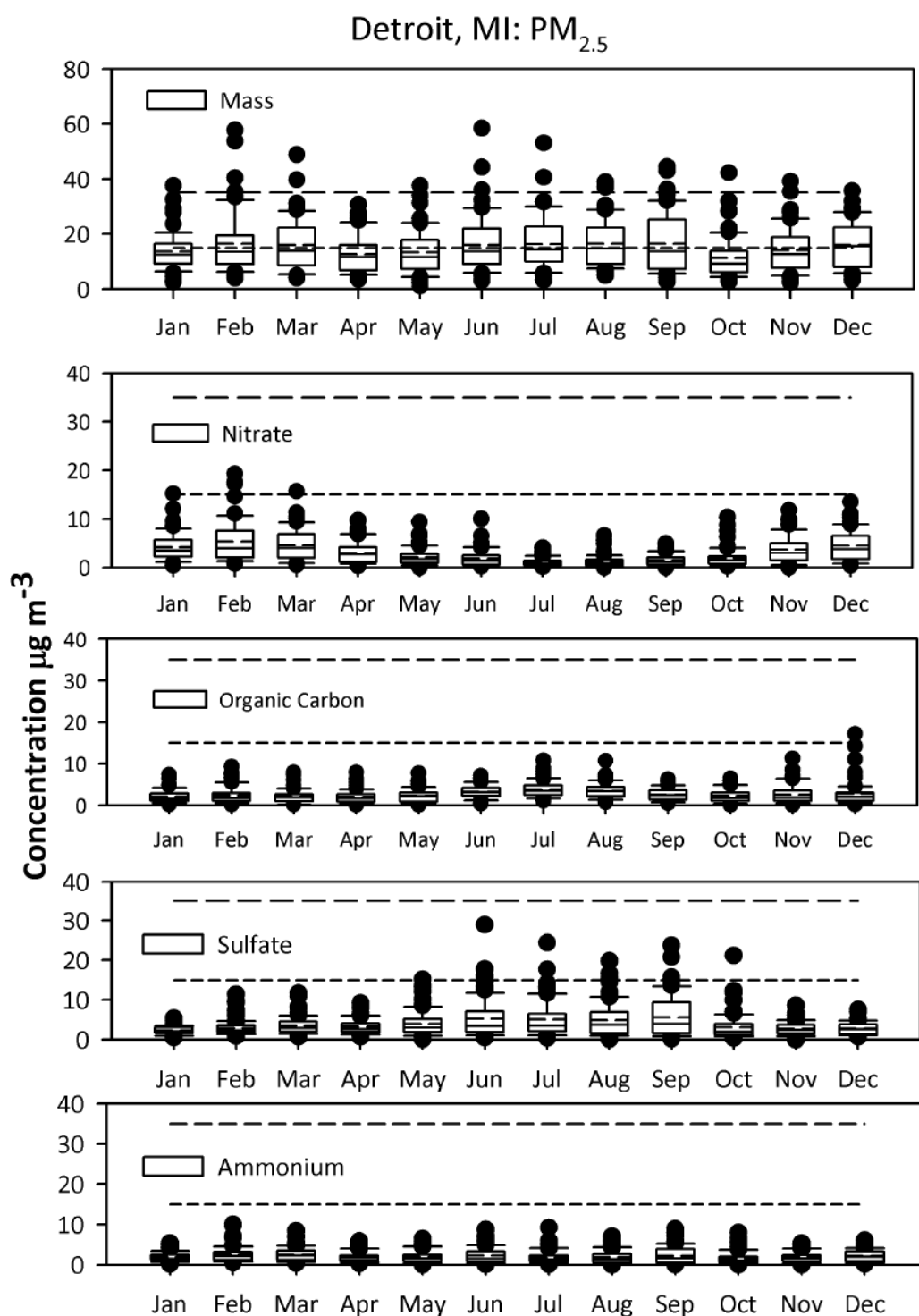


Fig. S3. Measurements of PM_{2.5} mass, nitrate, organic carbon, sulfate and ammonium made at Detroit, MI (see Table S1 for sampler numbers, and measurement dates) by the US Environmental Protection Agency using the Criteria Pollutants Network and the Chemical Speciation Network. The box plots show the 10th and 90th percentiles as whiskers, the 25th and 75th percentiles as the box ends, the median as a solid line intersecting the box, the mean as a dashed line, and the data beyond the 10th and 90th percentiles as individual measurements.

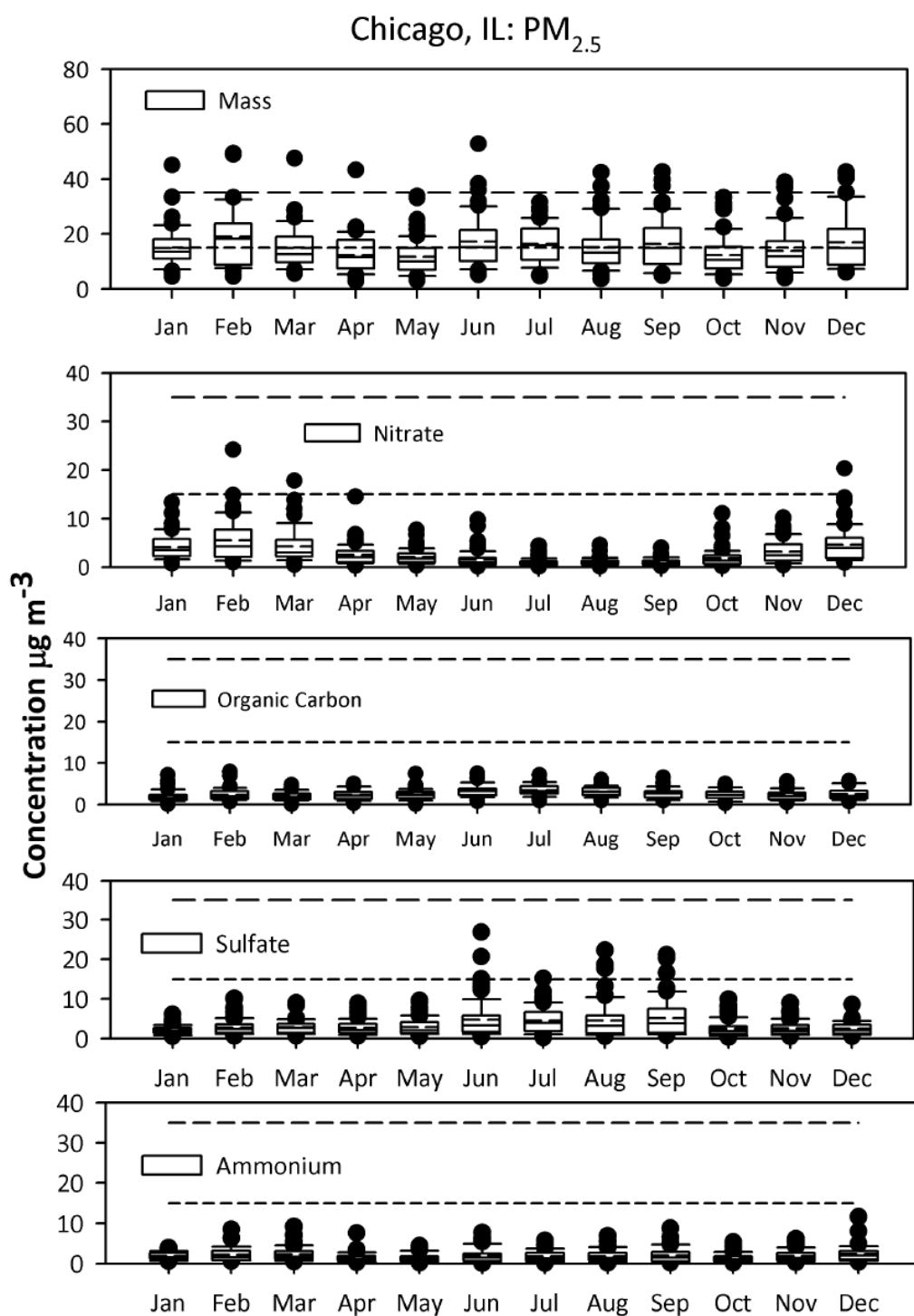


Fig. S4. Measurements of PM_{2.5} mass, nitrate, organic carbon, sulfate and ammonium made at Chicago, IL (see Table S1 for sampler numbers, and measurement dates) by the US Environmental Protection Agency using the Criteria Pollutants Network and the Chemical Speciation Network. The box plots show the 10th and 90th percentiles as whiskers, the 25th and 75th percentiles as the box ends, the median as a solid line intersecting the box, the mean as a dashed line, and the data beyond the 10th and 90th percentiles as individual measurements.

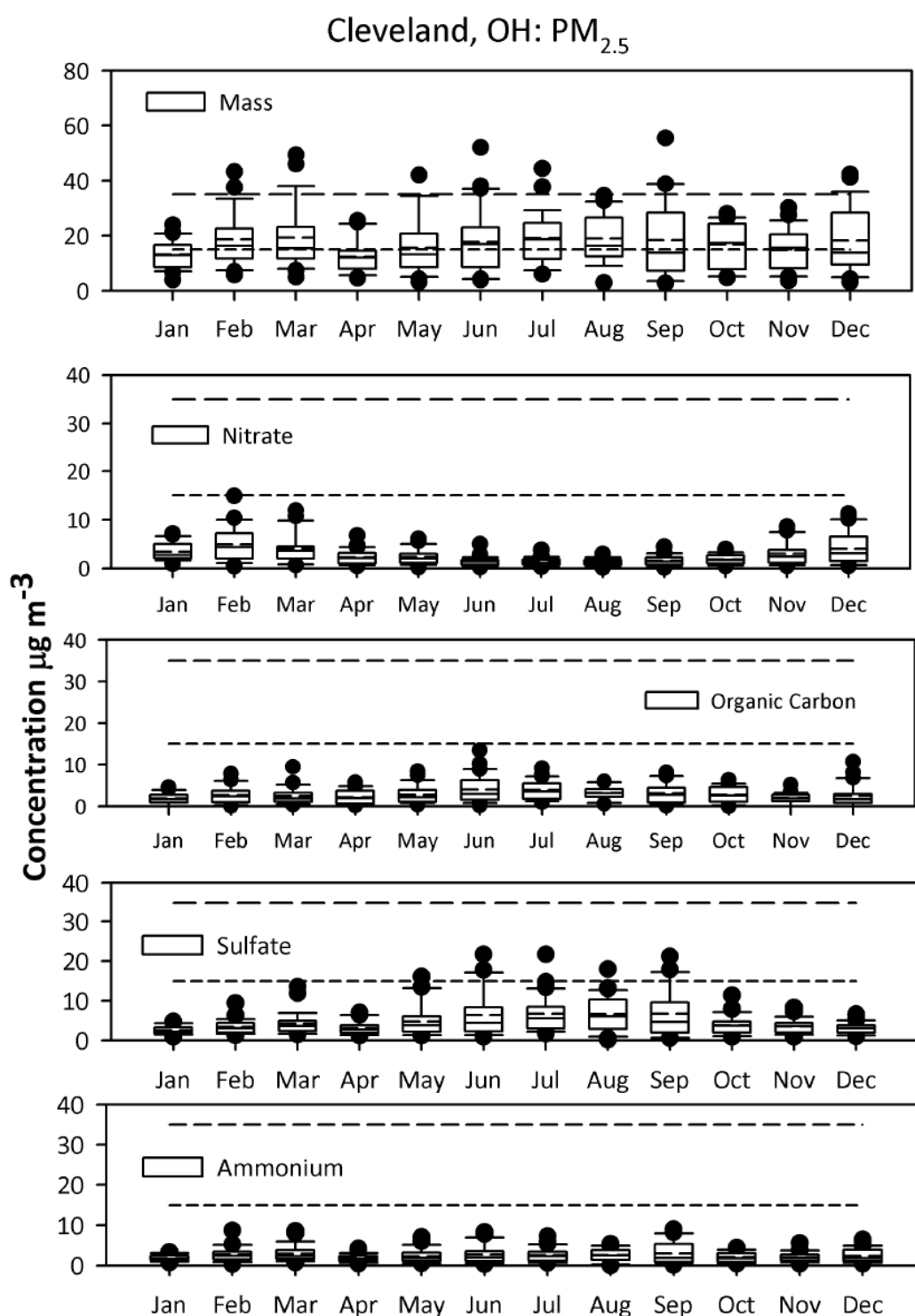


Fig. S5. Measurements of PM_{2.5} mass, nitrate, organic carbon, sulfate and ammonium made at Cleveland, OH (see Table S1 for sampler numbers, and measurement dates) by the US Environmental Protection Agency using the Criteria Pollutants Network and the Chemical Speciation Network. The box plots show the 10th and 90th percentiles as whiskers, the 25th and 75th percentiles as the box ends, the median as a solid line intersecting the box, the mean as a dashed line, and the data beyond the 10th and 90th percentiles as individual measurements.

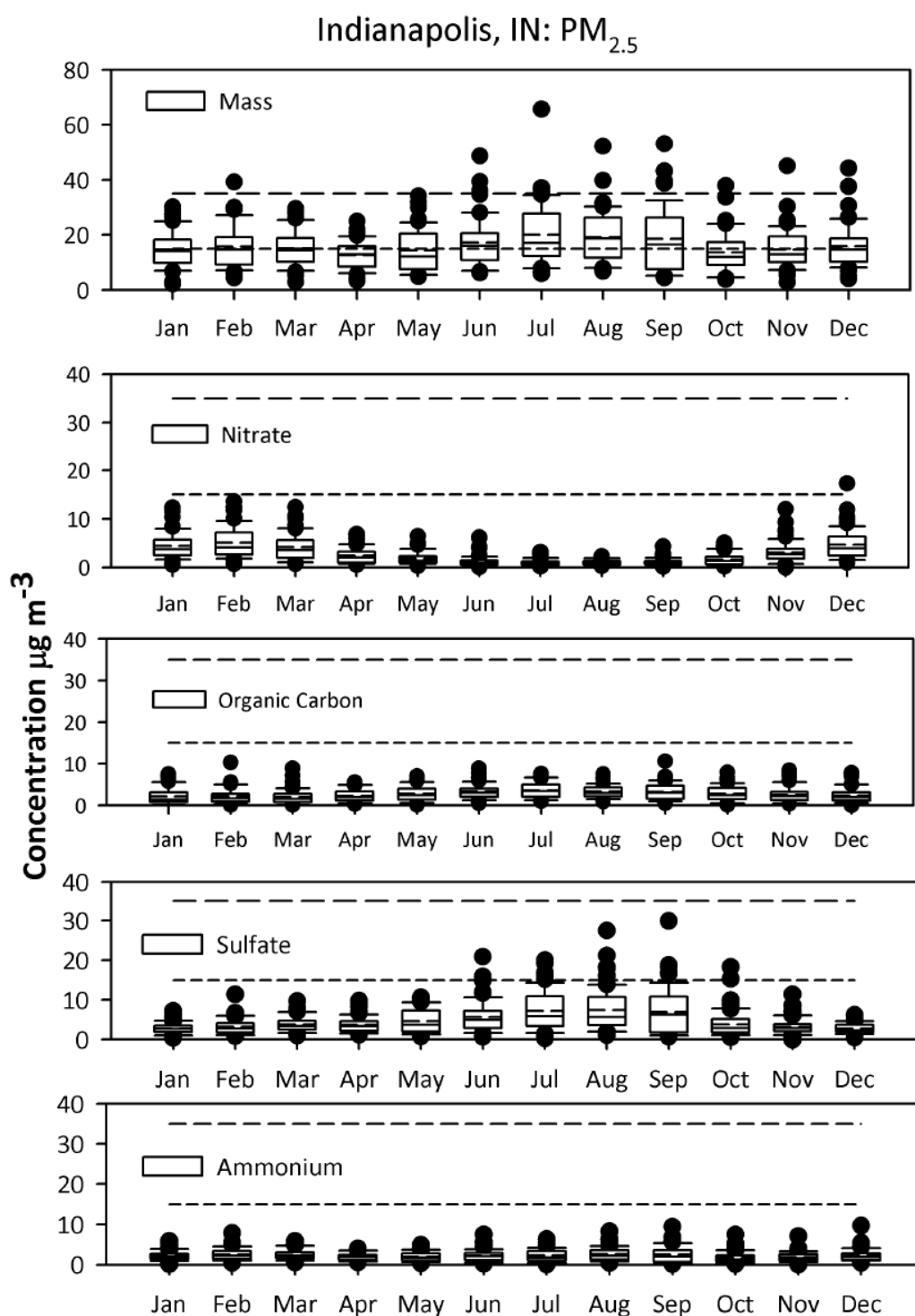


Fig. S6. Measurements of PM_{2.5} mass, nitrate, organic carbon, sulfate and ammonium made at Indianapolis, IN (see Table S1 for sampler numbers, and measurement dates) by the US Environmental Protection Agency using the Criteria Pollutants Network and the Chemical Speciation Network. The box plots show the 10th and 90th percentiles as whiskers, the 25th and 75th percentiles as the box ends, the median as a solid line intersecting the box, the mean as a dashed line, and the data beyond the 10th and 90th percentiles as individual measurements.

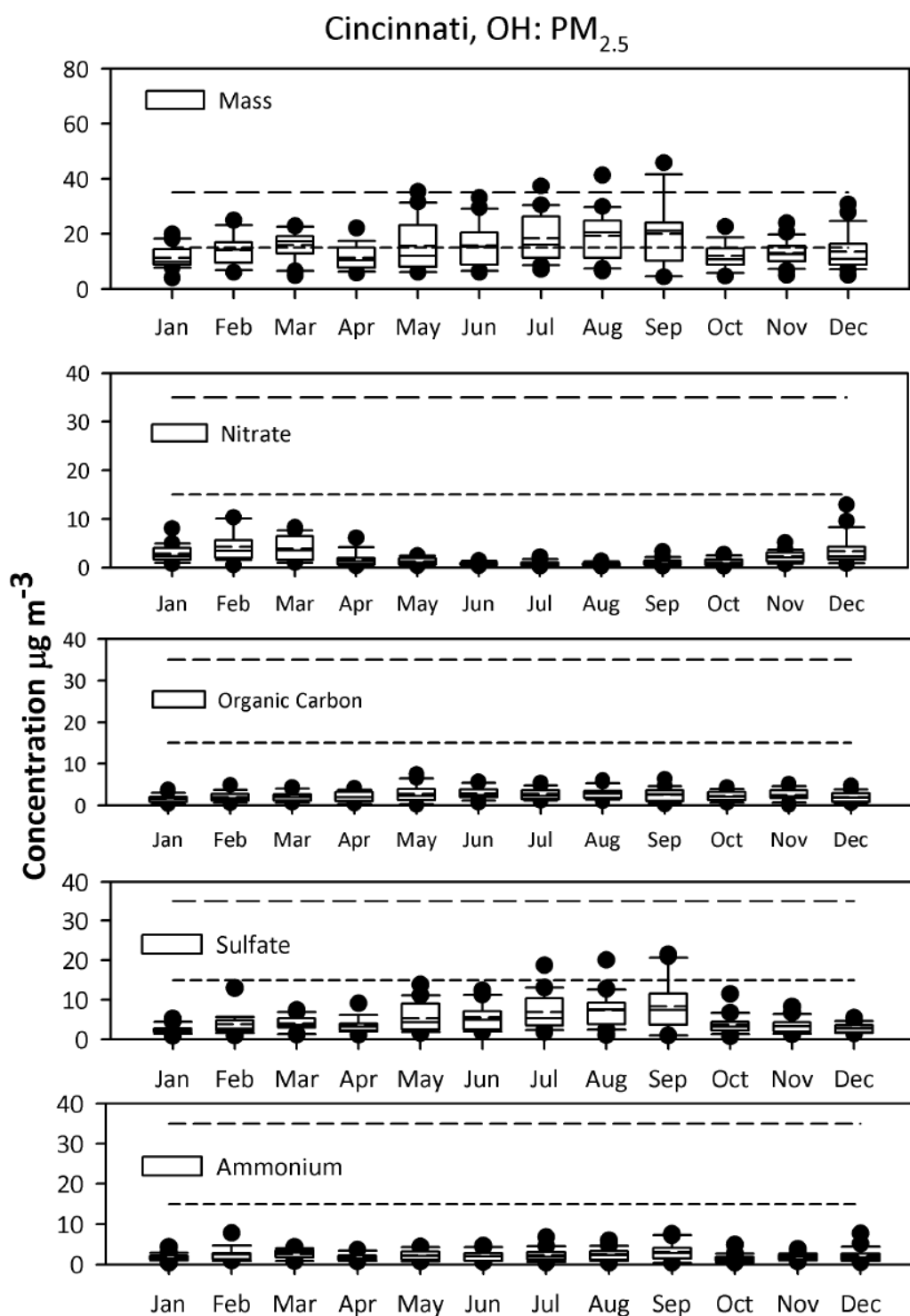


Fig. S7. Measurements of PM_{2.5} mass, nitrate, organic carbon, sulfate and ammonium made at Cincinnati, OH (see Table S1 for sampler numbers, and measurement dates) by the US Environmental Protection Agency using the Criteria Pollutants Network and the Chemical Speciation Network. The box plots show the 10th and 90th percentiles as whiskers, the 25th and 75th percentiles as the box ends, the median as a solid line intersecting the box, the mean as a dashed line, and the data beyond the 10th and 90th percentiles as individual measurements.

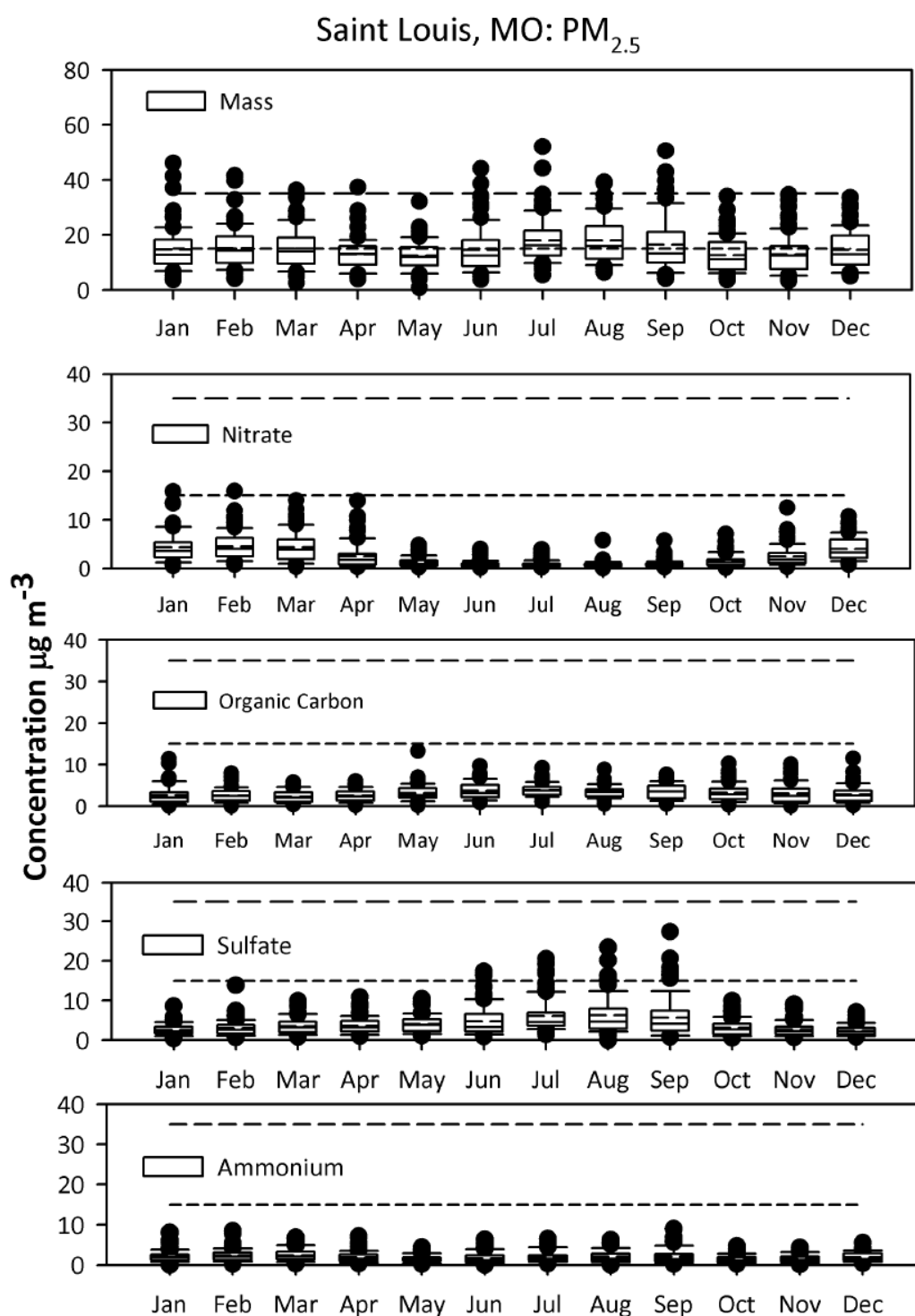


Fig. S8. Measurements of PM_{2.5} mass, nitrate, organic carbon, sulfate and ammonium made at Saint Louis, MO (see Table S1 for sampler numbers, and measurement dates) by the US Environmental Protection Agency using the Criteria Pollutants Network and the Chemical Speciation Network. The box plots show the 10th and 90th percentiles as whiskers, the 25th and 75th percentiles as the box ends, the median as a solid line intersecting the box, the mean as a dashed line, and the data beyond the 10th and 90th percentiles as individual measurements.

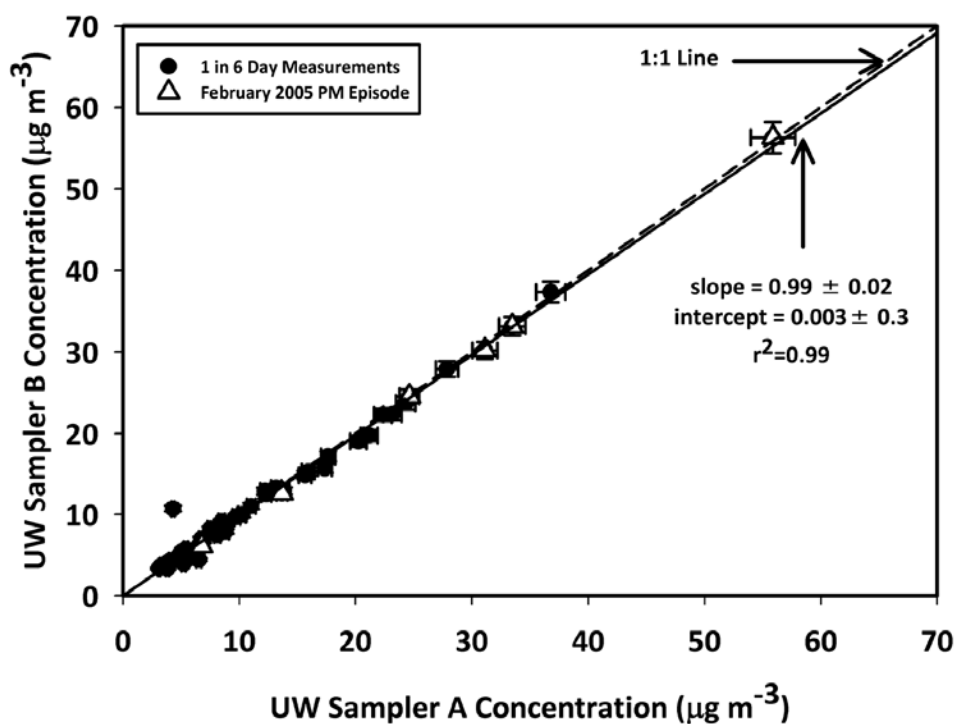


Fig. S9. A comparison mass measurements made using the two UW-Madison PM_{2.5} sampling channels at Milwaukee, WI. The samplers were operated on 1-in-6 day schedules between June 2004 and May 2005, and on a daily basis between 1 and 4 February 2005 during the PM episode.

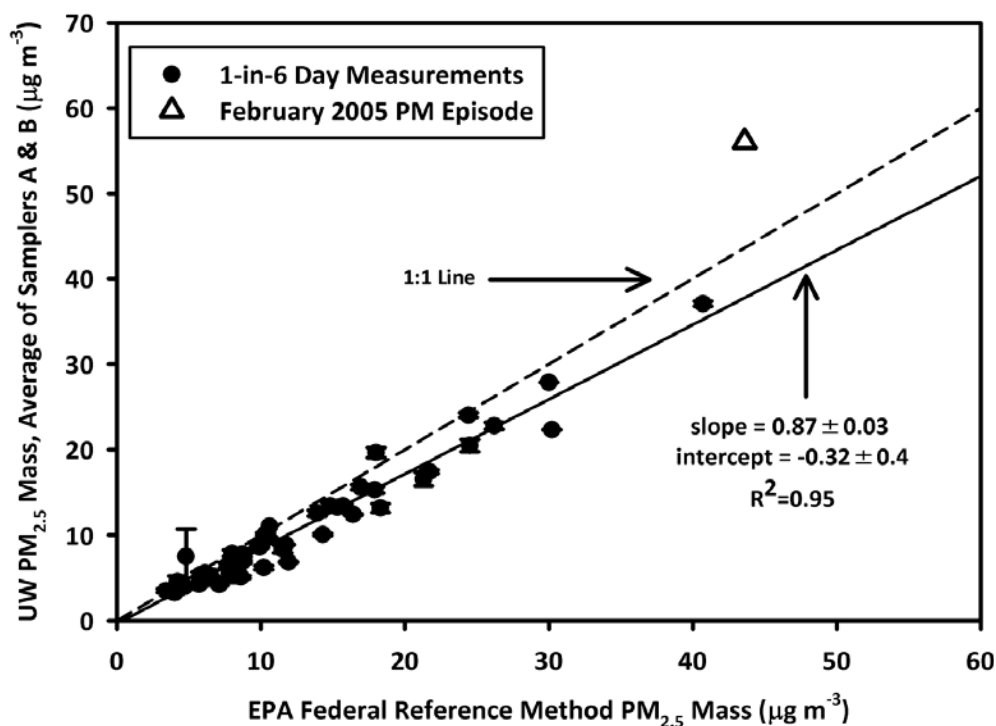


Fig. S10. A Comparison of PM_{2.5} mass measurements made by the US EPA (FRM) and UW-Madison at Milwaukee, WI. Both samplers were operated on 1-in-6 day schedules between June 2004 and May 2005.

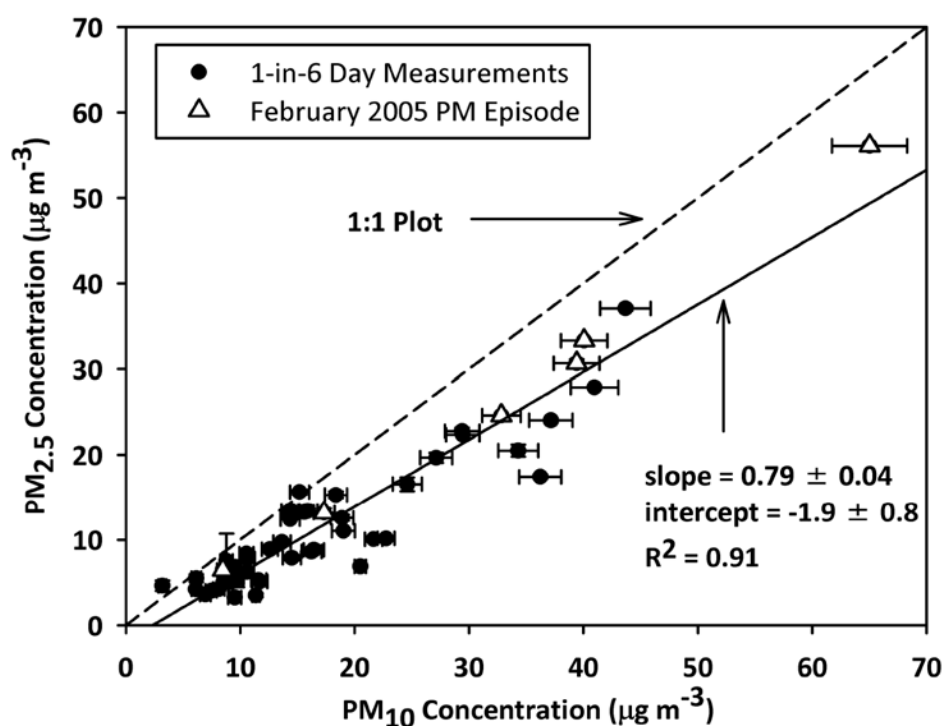


Fig. S11. A comparison of $PM_{2.5}$ against PM_{10} mass measurements made by UW-Madison at Milwaukee, WI. The samplers were operated on 1-in-6 day schedules between June 2004 and May 2005, and on a daily basis between 1 and 4 February 2005 during the PM episode.

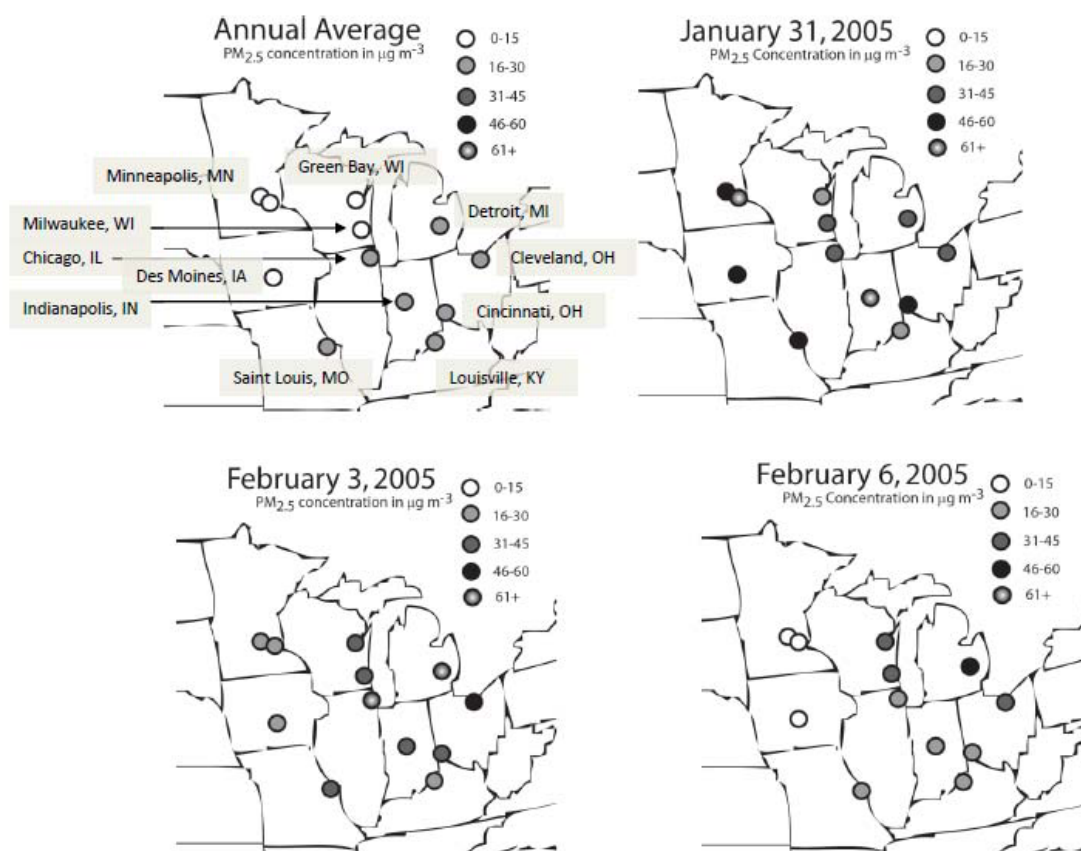


Fig. S12. $PM_{2.5}$ concentrations from each of the cities in the study. The figure presents the annual average and 1-in-6 day averages during the February 2005 PM episode.

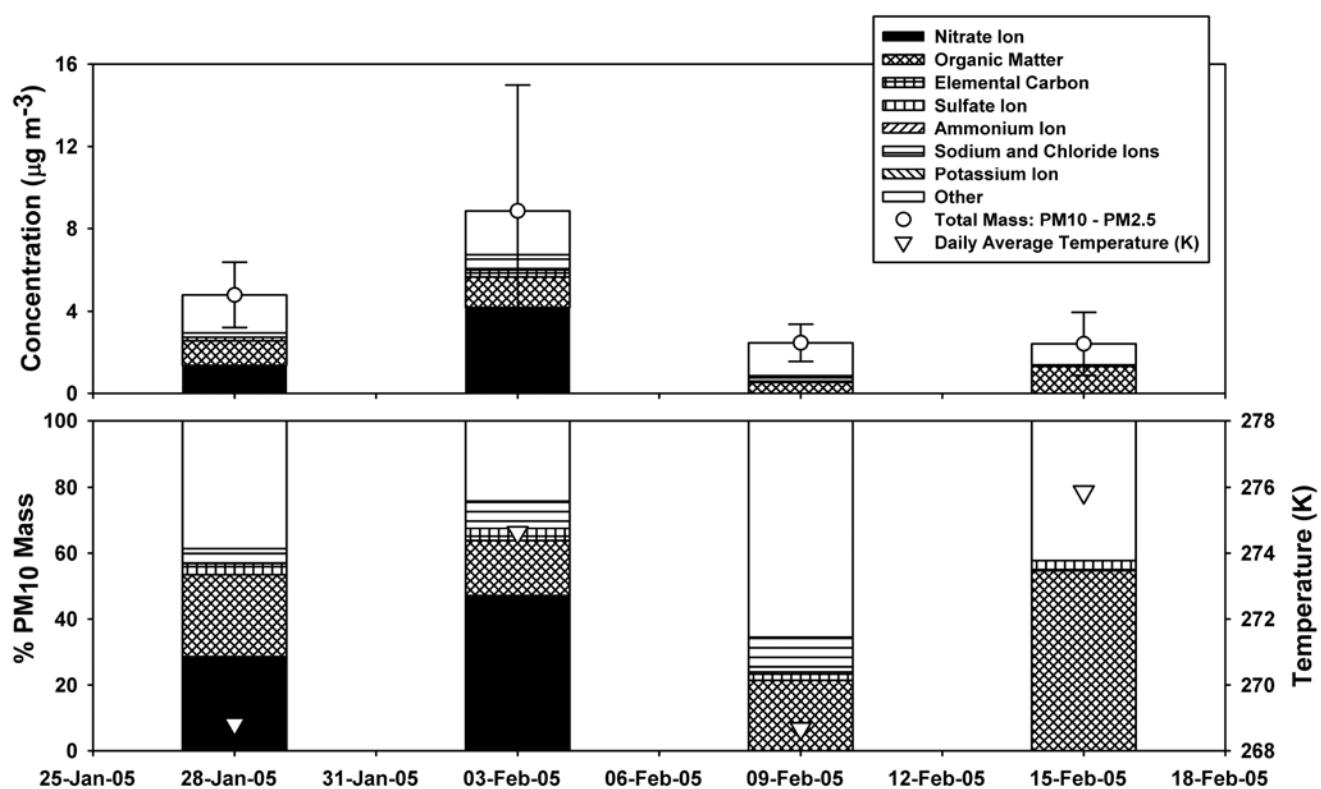


Fig. S13. Absolute and relative PM_{10-2.5} composition during the February 2005 high PM concentration episode at Milwaukee, WI.